



Sonoma Technology, Inc.
Air Quality Research and Innovative Solutions

A COMPARISON OF AMBIENT MEASUREMENTS TO EMISSIONS REPRESENTATIONS FOR MODELING TO SUPPORT THE CENTRAL CALIFORNIA OZONE STUDY (CCOS)

**FINAL REPORT
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EXECUTIVE SUMMARY

This study was sponsored by the San Joaquin Valley Air Pollution Study Agency (SJVAPSA) in support of the Central California Ozone Study (CCOS), a multi-year program of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. The CCOS was initiated for the purpose of improving the scientific understanding of ozone air quality problems in northern and central California. The goals of the CCOS are being met through analysis of existing data; a large-scale field study conducted in summer 2000 to acquire a comprehensive database to support modeling and data analysis; analysis of the data collected during the field study; and the development, evaluation, and application of air quality modeling capabilities for northern and central California. This project, A Comparison of Ambient Measurements to Emissions Representations for Modeling, complements other CCOS activities. Sonoma Technology, Inc. (STI) investigated why preliminary CCOS photochemical modeling results differ from ambient observations by comparing emissions and ambient data. The objective of this project is to provide corroborative evidence, with sufficient justification, that can potentially explain differences between modeled and observed pollutant concentrations.

Several techniques were used to evaluate CCOS emissions data and make comparisons between emission inventory estimates and ambient data:

- An evaluation of the availability, quality, and representativeness of air quality and meteorological data collected during the CCOS period (summer 2000).
- A review of the total organic gas (TOG) speciation profiles used by ARB to prepare emission inventories for air quality model runs.
- A reconciliation of emissions data and ambient data by comparing emission inventory- and ambient-derived pollutant ratios.
- A “fingerprint analysis” performed by comparing emission inventory- and ambient-derived compositions of total non-methane organic carbon (TNMOC).
- A review of the methodologies used to model emissions from two large wildfires that occurred in the CCOS modeling domain during the July 29–August 3, 2000, ozone episode.
- Source apportionment analyses performed on ambient data from three monitoring sites in Central California.

These techniques were primarily applied to ambient and emission inventory data from central California air basins due to the limited availability of ambient measurements from San Francisco Bay Area sites. Overall, the results of this project indicate that the methodologies used by ARB and the local air districts to estimate, spatially and temporally allocate, and chemically speciate emissions are resulting in improved emission inventories. This conclusion is bolstered by the fact that the comparisons between ambient and emission inventory data performed during this project show closer agreement than similar comparisons performed during earlier studies in central California. For example, **Figure ES-1** shows that the ratio between ambient- and emission inventory-derived TNMOC/oxides of nitrogen (NO_x) ratios for the First Street site in

Fresno improved from 2.7 to 1.3 between the summers of 1996 and 2000, while the ratio of carbon monoxide (CO)/NO_x ratios improved from 2.6 to 1.7.

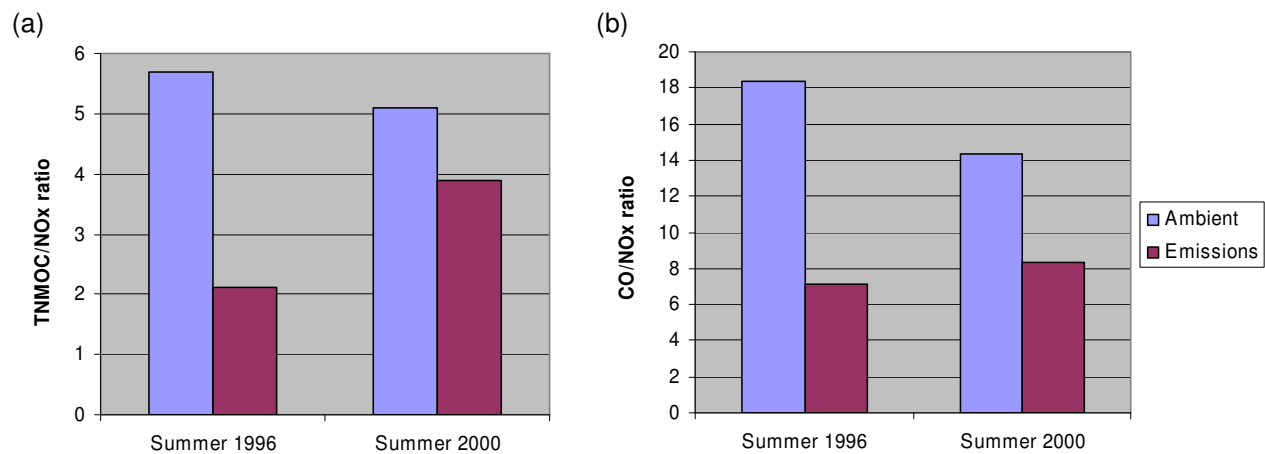


Figure ES-1. Trends in ambient- and emission inventory-derived (a) TNMOC/NO_x and (b) CO/NO_x ratios at the Fresno First Street site.

In addition, the analyses conducted in this project identified several specific improvements that could be made to existing emission estimates. The most significant recommendations (in terms of likely impact on overall emission estimates and modeling results) are to

- Improve the accuracy of weekend motor vehicle activity estimates to better characterize differences in weekday and weekend-day travel. Resulting improvements in emission estimates would likely be a particular benefit in the Sacramento area, where comparisons between ambient and emission inventory data show less agreement on weekend days than on weekdays.
- Further investigate the poor agreement between ambient and emission inventory data in Kern County. Comparisons between ambient and emission inventory data indicate that TNMOC emissions are underestimated at Bakersfield, and that mobile sources are underrepresented in the emission inventory at Bakersfield. Source apportionment results indicate that mobile sources account for about 60% of the identified TNMOC mass at the Bakersfield Golden State monitoring site, while the emission inventory for the area around that monitoring site attributes less than half of TNMOC emissions to mobile sources.
- Correct the vertical distribution of wildfire emissions, which are a significant source of TOG and NO_x emissions during the July/August 2000 ozone episode (for example, on July 31, 2000, TOG emissions from wildfires were estimated to be 1,988 tons per day, or about 50% of the total TOG emissions from all anthropogenic sources).

It should also be noted that the ARB and local air districts are acting on other recommendations made by STI, such as improvements to individual speciation profiles and a correction to the spatial distribution of emissions from livestock waste.

A detailed description of the methodologies and data sets used to perform various comparisons of ambient and emission inventory data and the findings and recommendations resulting from each comparison have been documented in a series of technical memoranda. The documents are included in this final report as appendices, and the findings from each analysis technique are summarized in Sections ES.1–ES.6.

ES.1 RESULTS OF AIR QUALITY DATA EVALUATION

STI investigated the available monitoring sites in the CCOS domain to identify potential sites collecting ambient data of sufficient quality and quantity for comparison with emission inventory data. The pollutants and parameters of interest included volatile organic compounds (VOC), NO_x, CO, and meteorological data collected during the summer 2000 ozone season.

To prioritize sites for inclusion in subsequent analyses, STI considered numerous criteria for several dozen air quality monitoring sites in the CCOS domain, including the availability of speciated VOC measurements; the availability of NO_x, CO, and TNMOC measurements; the number of values above detection limits and background thresholds; and the density of ozone precursor emissions in the area surrounding each monitoring site.

Examination of the site measurements relative to the criteria resulted in a grouping of the sites into five distinct “tiers.” Five sites met all the selection criteria and were denoted Tier 1 (most suitable ambient data for comparison with emission inventory data). Two sites failed one of the selection criteria and were denoted Tier 2. Seven more sites failed two of the criteria and were denoted Tier 3 (Tiers 2 and 3 sites are typically less suitable for comparison because of low emissions near the site or insufficient measurements). Sites at which no speciated VOC data were available but at which some CO or TNMOC measurements were made were also considered less suitable (Tiers 4 and 5). All other sites were considered unsuitable for analysis. Appendix A provides a more detailed description of the data available from each monitoring site, and **Figure ES-2** shows the location and tier designation of each site.

ES.2 RESULTS OF SPECIATION PROFILE REVIEW

STI reviewed the speciation profiles used by the ARB to prepare emission inventories for photochemical air quality modeling efforts. Speciation profiles provide a detailed breakdown of the individual chemical species emitted by a specific source category. Incorrect assignments of speciation profiles to emissions sources and/or speciation profiles that do not accurately represent the chemical composition of emissions can cause inaccuracies that may impact photochemical modeling results.

ARB provided STI with the library of TOG speciation profiles used in preliminary CCOS modeling efforts, as well as a cross-reference file that matches each source category in the CCOS emission inventory with a TOG speciation profile. STI reviewed the speciation profiles, profile-to-source category assignments, and supporting literature and documentation and performed a literature search to identify improved speciation data. As part of this assessment, STI also ranked the relative importance of the 425 TOG speciation profiles provided by ARB, based on the mass and reactivity of emissions associated with source categories assigned to each profile.

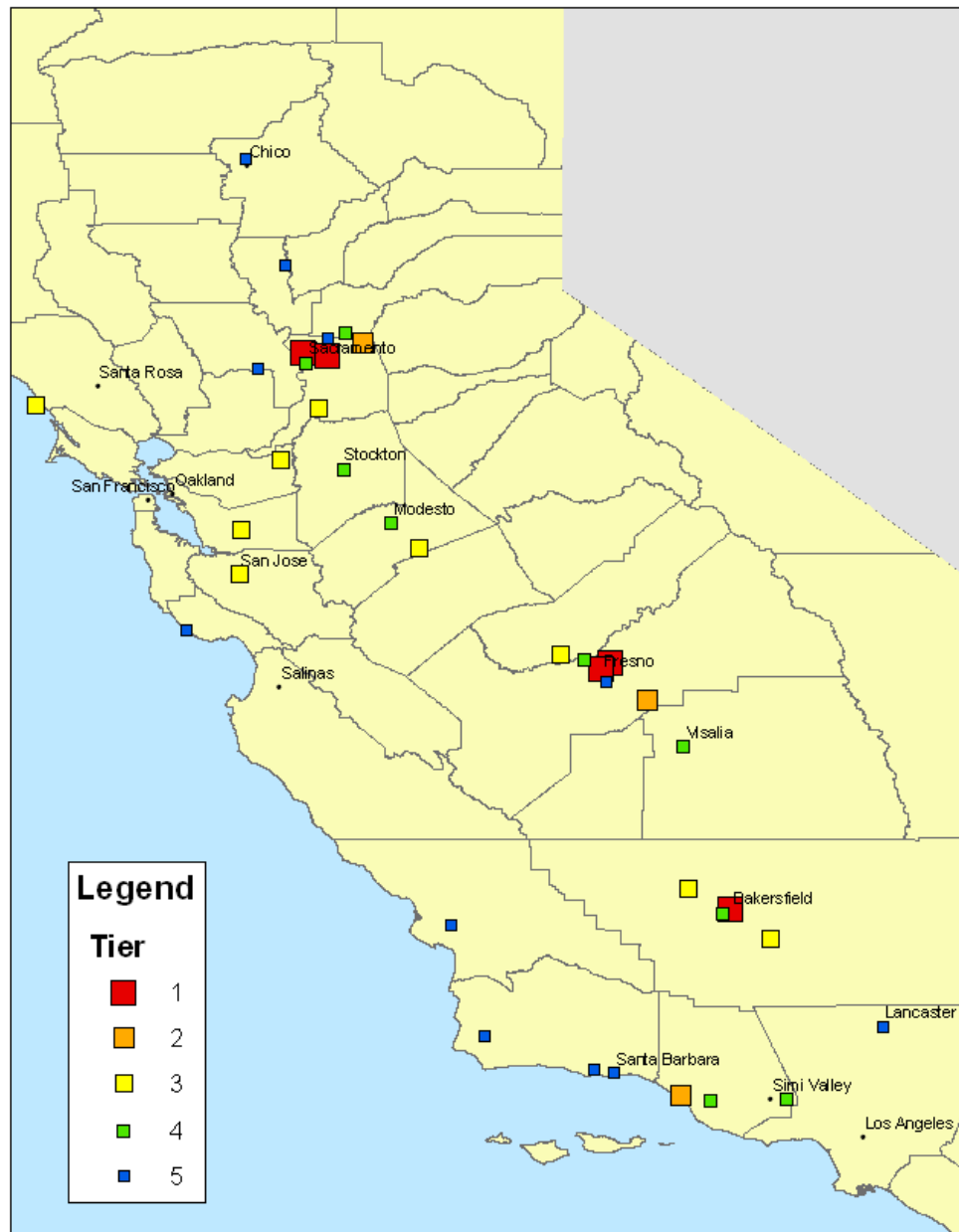


Figure ES-2. Map of air quality sites and tier designations.

A major finding of these analyses is that only a handful of the ARB organic gas speciation profiles appear to significantly affect the preparation of the CCOS emission inventory for modeling. Ten profiles account for 80% of the reactivity-weighted TOG emissions in the CCOS inventory, which greatly narrows the focus for pending speciation profile research and improvements. Specific findings and recommendations related to these 10 high-priority (and other) profiles, as well as ARB's response to these recommendations, are listed in **Table ES-1**. Appendix B provides a detailed description of the techniques and findings associated with this task.

Table ES-1. Recommendations for improvements to ARB speciation profiles.

Profile #	Profile Name	STI Recommendation	ARB Response
401	Gasoline - non-catalyst - stabilized exhaust	For off-road mobile sources, use 1997 Gabele ^a lawnmower profile.	ARB staff recommends that the Gabele ^a profile should be applied to less than 25 hp engines and the current profile for non-catalyst on-road engines be used for larger engines. ARB staff are in the process of reviewing off-road emission inventory code (EIC) categories to determine if they are predominantly less than or greater than 25 hp. The appropriate speciation profile will be assigned accordingly.
818	Diesel farm equipment	For on-road mobile sources, use 1999 Schauer ^b diesel exhaust profile.	ARB plans to incorporate the Schauer ^b diesel exhaust profile.
203	Animal waste decomposition	Further study needed to assess fraction of reactive organic gas (FROG) by manure-handling process.	California State University at Fresno is currently under contract with ARB to conduct tests to develop chemical speciation at California dairies. The profile developed will be used when available.
586	Composite jet exhaust	Further study needed to develop a jet exhaust profile that reflects current fuel compositions.	In 2006, ARB and others participated in the JETS experiment in which Boeing 737 engines at the Oakland airport were tested. The results of this project and recent testing by other parties will be analyzed to determine the data's suitability for use in developing a new speciation profile.
307	Forest fires	Further study needed to develop a composite speciation profile that reflects the dominant biomass types in California.	ARB recently proposed that chemical speciation be developed from the combustion of five dominant California plant species. A new profile for wildfires will be developed if this study is approved.
783	Industrial surface coatings	Use 2005 Lake Michigan Air Directors Consortium (LADCO) profiles which reflect current solvent compositions.	ARB is investigating the appropriateness of the LADCO profiles.
716	Medium cure asphalt	Further study needed to develop a new speciation profile from current asphalt samples.	ARB agrees that further study would be beneficial. However, no studies are planned at this time.
600	All category composite	Develop multiple composite profiles by broad source types such as fuel combustion and solvent usage.	ARB will incorporate this recommendation as resources are available.

^a Gabele P. (1997) Exhaust emissions from four-stroke law n mower engines. *J Air Waste Manag Assoc.* **47**, 945-952.

^b Schauer J.J., Kleeman M.J., Cass G.R., and Simoneit B.R.T. (1999) Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks. *Environ. Sci. Technol.* **33** (10), 1578-1587.

ES.3 RESULTS OF POLLUTANT RATIO COMPARISON

STI performed an inventory reconciliation analysis by making a selective, quantitative comparison of emission inventory- and ambient-derived molar pollutant ratios (e.g., TNMOC/NO_x, CO/NO_x, and individual hydrocarbon species such as benzene/toluene).

Emissions reconciliation requires careful selection of data sets to minimize the effects of confounding factors such as the transport of aged pollutants from distant sources and the transformation of fresh pollutants by chemical reactions. These factors can be minimized by applying emissions reconciliation techniques to data from monitoring sites that are likely to be impacted by local sources rather than by transported pollutants (i.e., sites in urban areas) and by selecting time periods when chemical reaction rates are low (e.g., morning hours from 0500-1000). Under these conditions, emission rates are high, mixing depths are low, and long-range transport and chemical reactions are minimal. However, because of the inherent uncertainties associated with this analysis method, it should be noted that ambient- and emission-derived ratios that are within approximately 25-50% of each other are considered to be in good agreement (California Air Resources Board, 1997).

STI selected data sets that met the conditions described above and computed molar-based pollutant ratios from ambient and emission inventory data for direct comparison. Comparisons of TNMOC/NO_x and individual hydrocarbon species ratios were performed for 11 sites, and comparisons of CO/NO_x ratios were performed at for 8 sites. Where possible, comparisons were made by wind quadrant (based on predominant wind speeds during the early morning hours) and for both weekdays and weekend days. Key findings and recommendations that resulted from this emissions reconciliation are summarized below:

- When compared with previous emissions reconciliation studies, the emission inventory data used in this project are generally in better agreement with ambient data than are date previous emission inventory data.
- At some sites, the emission inventory data correlate with ambient data as closely as could be expected, given the limitations of the comparison techniques used; the ratio of ambient- to emission inventory-derived pollutant ratios is generally 1.5 or less).
- For urbanized areas in the northern part of the CCOS modeling domain (the Sacramento area), the gridded emission inventory data are in good agreement with data from ambient monitoring sites on weekdays (i.e., the ratio of ambient- to emission inventory-derived pollutant ratios is 1.5 or less), but show poorer agreement on weekend days.
- For urbanized areas in the central part of the CCOS modeling domain (the Fresno area), the gridded emission inventory data are generally in good agreement with data from ambient monitoring sites on both weekdays and weekend days.
- For urbanized areas in the southern part of the CCOS modeling domain (Kern County), the gridded emission inventory data do not show good agreement with ambient monitoring data on either weekdays or weekend days.
- For most rural areas in the CCOS modeling domain, the gridded emission inventory data do not show good agreement with ambient monitoring data on either weekdays or weekend days. However, these sites do not fully meet the underlying assumptions of the

analysis techniques used (i.e., there are significant local emissions around a monitoring site).

Based on the findings from this study, STI recommends that the following steps be taken to further investigate the CCOS modeling emission inventories and to make specific improvements to those inventories:

- Improve the accuracy of weekend emission estimates in the Sacramento area. Because monitoring sites in Sacramento are likely to be primarily influenced by on-road mobile source emissions, weekend vehicle activity data should be collected and used to better characterize differences in weekday and weekend-day travel.
- Further investigate the poor agreement between ambient and emissions data in Kern County. Because the comparison between ambient and emissions data is generally good at urban sites dominated by mobile sources, other source types may be poorly characterized in Kern County. Bottom-up efforts to “ground truth” the Kern County emission inventory could be used to identify specific areas of improvement.
- Collect more ambient data at San Francisco Bay Area (SFBA) sites. The possible comparisons between ambient and emission inventory data were very limited in this project given the lack of available data from SFBA sites.

A detailed description of the analysis techniques and results that served as the basis for these conclusions and recommendations are provided in Appendix C.

ES.4 RESULTS OF FINGERPRINT ANALYSIS

In addition to ratio comparisons, STI compared the chemical composition of hydrocarbons reported in the emission inventory to the chemical composition of ambient air at individual monitoring sites. These “fingerprint” analyses were used to determine how accurately the speciation in the emission inventory compares to the data collected at ambient monitoring sites. Hydrocarbon compositions were based on species groupings defined by ARB’s modeling emissions data system (MEDS) (Allen, 2001), and the species measured at each monitoring site were assigned to one of these groups for purposes of comparison.

Comparisons of the ambient- and emission inventory-derived relative hydrocarbon compositions were performed for 10 sites. In general, the fingerprint analyses showed that

- The speciation of the emission inventory is representative of the TNMOC composition detected by ambient monitoring sites for most species groups.
- The contribution of ethane to the overall TNMOC composition is consistently higher in the emission inventory than in the ambient data. Further analysis of the emission inventory showed that this overprediction is attributable to emissions from livestock waste. (In a related CCOS study [Chinkin and Reid, 2006], STI discovered that significant amounts of livestock waste emissions were spatially distributed across the CCOS modeling domain using human population as a spatial surrogate. ARB has subsequently addressed this issue.)

- The contribution of propane to the overall TNMOC composition is consistently lower in the emission inventory than in the ambient data. These differences may be due to the fact that propane has a low reactivity and tends to persist in the atmosphere. However, these differences may also indicate an underprediction of emissions from oil and natural gas extraction and production activities, which are a significant source of propane. This conclusion is bolstered by the fact that other species emitted by oil and gas production activities, such as butanes and pentanes, also tend to be underpredicted in the emission inventory (though these more highly reactive compounds are underpredicted by a smaller amount than is propane).
- The contribution of isoprene to the overall TNMOC composition is consistently higher in the emission inventory than in the ambient data. However, this difference is likely due to the fact that isoprene, a highly reactive species, is being removed from the ambient air by photochemistry before it can be detected at monitoring sites.

A detailed description of the fingerprint analysis techniques and results are provided in Appendix C.

ES.5 RESULTS OF WILDFIRE EMISSIONS REVIEW

STI reviewed the methodologies ARB used to model emissions from two large wildfires that occurred in the CCOS modeling domain during the July 29–August 3, 2000, ozone episode. The Manter fire burned a 73,000-acre area in Tulare County from July 22–August 8, 2000, and the Plaskett fire burned a 58,000-acre area in Monterey County from July 23–31, 2000. The timing and scale of these fires prompted ARB staff to estimate daily emissions from these fires in order to assess their potential impact on regional photochemistry (Scott, 2003). ARB provided STI with air quality model-ready (i.e., gridded, hourly, vertically distributed) point source emission files that included wildfire emissions. STI analyzed the spatial and temporal characteristics of the wildfire emission estimates and evaluated alternative methods and data sets that could be used to improve the characterization of model-ready wildfire emissions.

STI found that, in general, emissions from the Manter and Plaskett fires were reasonably estimated on a daily scale, given the available data. However, issues do exist with the temporal, spatial, and vertical distribution of emissions—due in part to the way emissions from the flaming and smoldering phases of fires were combined and treated identically in time and space. However, smoldering combustion is lower in intensity than flaming combustion, which results in the smoldering phase having a longer duration and resulting in less lofted smoke than the flaming phase. This finding has implications:

- The diurnal profile applied to wildfire emissions may not adequately take into account the duration of smoldering emissions, resulting in an underestimate of emissions (particularly TOG) during night and morning hours.
- Accounting for the longer duration of smoldering emissions would change the relative spatial distribution of TOG and NO_x emissions during a multi-day burn, as TOG-rich smoldering emissions from the previous day's burn "footprint" would be incorporated into emission estimates for subsequent days.

In addition, it was determined that the methods used to vertically distribute wildfire emissions within the Comprehensive Air Quality Model with extensions (CAMx) resulted in a plume rise of well over 10 km from the Manter fire. Fires were treated as point sources within the model, using the stack height parameter to set the vertical level of wildfire emissions for a given hour and grid cell. However, because of the settings used for other stack parameters (such as stack temperature and exit velocity), an internal plume rise calculation performed by CAMx resulted in emissions being lofted several kilometers higher than was originally intended.

Based on the findings outlined above, STI makes the following recommendations for improving the characterization of wildfire emissions and for conducting further investigations:

- Stack parameters assigned to wildfires should be set to levels that ensure that no plume rise is calculated within CAMx.
- Fire emission estimates should be adjusted to account for ongoing “second day” smoldering emissions (this step would also alter the spatial distribution of emissions).
- A U.S. Environmental Protection Agency diurnal profile for wildfires that takes into account “second day” smoldering emissions may be more representative of total hourly emissions (flaming plus smoldering) than the current temporal profile.

A detailed description of the techniques used to analyze wildfire emissions and the resulting findings and recommendations are provided in Appendix D.

ES.6 RESULTS OF SOURCE APPORTIONMENT ANALYSES

STI conducted source apportionment analyses using the positive matrix factorization (PMF) and chemical mass balance (CMB) receptor models. These analyses were performed using ambient air quality data from three monitoring sites in the CCOS domain: Sacramento Del Paso Manor (SDP), Clovis (CLO), and Bakersfield Golden State (BGS). The goals of these analyses were to (1) determine relative emissions source contributions to total TNMOC mass observed in the ambient air, and (2) to assess how well the source contributions identified using receptor models compare to TNMOC emission breakdowns by source category in the emission inventory (EI).

Among the three monitoring sites evaluated, ambient TNMOC concentrations were highest at the Bakersfield site, exceeding TNMOC concentrations at the Sacramento and Clovis sites by about 75% and 45%, respectively. However, the TNMOC emission inventory for the grid analysis zone around each monitoring site shows that TNMOC emissions are lowest at the Bakersfield site and highest at the Sacramento site. Because the EI reconciliation work showed relatively good agreement between the EI and ambient data at the Sacramento site, this finding indicates that the overall TNMOC inventory is likely to be underpredicted at both the Clovis and Bakersfield sites. Other findings emerged from the source apportionment analyses:

- At the Sacramento site, when the breakdown of identified TNMOC from the source apportionment analyses was plotted against results from the EI, the mobile source contributions from the EI (61%) fell within the range of mobile source TNMOC contributions from PMF (50%) and CMB (66%). These results corroborate the findings

from the EI reconciliation work, which indicated that the EI and ambient data showed relatively good agreement at the Sacramento site.

- At the Clovis site, stationary sources contributed almost 60% of total TNMOC emissions in the EI, while the source apportionment results suggest that over 60% of the identified TNMOC mass is mobile in origin.
- At the Bakersfield site, the EI shows less than half of TNMOC emissions attributed to mobile sources, while the source apportionment results suggest that mobile sources account for 55% to 61% of the identified TNMOC mass.

These results indicate that TNMOC emissions are underestimated at Bakersfield, and that mobile sources are underrepresented at Clovis and Bakersfield. A detailed description of the techniques used to conduct source apportionment analyses and the resulting findings and recommendations are provided in Appendix E.

ES.7 REFERENCES

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APPENDIX A

AIR QUALITY SITE SELECTION DECEMBER 13, 2005

TECHNICAL MEMORANDUM

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December 13, 2005

STI-905044.02-2866

To: Dr. Patricia Velasco, California Air Resources Board

From: Lyle R. Chinkin, Senior Vice President, Stephen B. Reid, Project Manager, Emissions Assessment Group, and Michael C. McCarthy, Senior Air Quality Analyst

Re: CCOS Task 2 – Air Quality Site Selection

As part of the Central California Ozone Study (CCOS) “Comparison of Ambient Measurements to Emissions Representations for Modeling”, Sonoma Technology, Inc. (STI) investigated the available monitoring sites to identify potential sites collecting ambient data of sufficient quality and quantity for comparison with emission inventory data. The ambient data comparisons will be used to make specific recommendations for emission inventory improvements that will improve photochemical modeling results. This technical memorandum summarizes the ambient data availability at sites in the CCOS domain and prioritizes the sites based on various objective criteria.

The pollutants and parameters of interest include ozone precursors (e.g., hydrocarbons and oxides of nitrogen [NO_x]) as well as carbon monoxide (CO) and meteorological data. **Table 1** lists the number of morning (0400 to 1000 PST) volatile organic compound (VOC), NO_x, CO, total nonmethane organic carbon (TNMOC), and wind direction samples collected from all sites during the 2000 summer ozone season in the CCOS domain. In addition, Table 1 provides the total organic gas (TOG) and NO_x emissions from a 14-km² area around each monitoring station from the “placeholder” gridded CCOS emission inventory.

To help prioritize the monitoring sites for possible inclusion in the Phase II analyses, we considered the following criteria for several dozen air quality sites in the CCOS domain:

- Availability of speciated VOC measurements
- Availability of NO_x measurements
- Availability of wind direction measurements
- Sufficient density of TOG and NO_x emissions

- Availability of CO or TNMOC measurements
- Number of distinct counts of VOC, NO_x, and CO (i.e., how many unique levels are reported for these measurements; fewer distinct reported levels are less suitable for analysis)
- Number of values above detection limit and background thresholds. For this analysis, we used VOC > 50 ppbC, NO_x > 10 ppb, and CO > 0.150 ppm.
- Visual inspection of monitoring sites using imagery from “Google™ Earth”. Sites were examined for visual evidence of local emissions.

Examination of the site measurements relative to the criteria resulted in grouping the sites into five distinct groups (labeled Tier 1 through 5 in Table 1). All sites that collected speciated VOC data and NO_x measurements were classified as Tier 1, 2, or 3 (the most suitable sites for comparisons with emission inventory data). Only six sites met all the criteria listed above and they were denoted Tier 1. Two additional sites failed one of these criteria and were denoted Tier 2. Seven additional sites failed two of the criteria and were denoted Tier 3. Tiers 2 and 3 sites are typically less suitable for comparison because of low emissions near the site or insufficient measurements.

Sites with no speciated VOC data that had some CO or TNMOC measurements were also considered less suitable. Sites that collected more than 10 CO or TNMOC measurements, NO_x measurements, meteorology measurements, and urban-like emissions of TOG and NO_x were considered Tier 4. Those sites that failed one of these criteria were considered Tier 5. All other sites were considered unsuitable for analysis.

Figure 1 shows a map with the location and Tier designation for each site in Table 1. Figures 2-31 show maps with the locations at two resolutions for each Tier 1, 2, and 3 site in Table 1. The most suitable sites for this analysis are all located in the San Francisco Bay Area or in the three major urban areas in the Central Valley (e.g., Sacramento, Fresno, and Bakersfield). Table 2 summarizes by date the availability of air quality data and includes both Photochemical Assessment Monitoring Stations (PAMS) data and additional measurements made during CCOS intensive operating periods (IOPs).

Table 1. Summary of measurement sites collecting data considered for comparison with emission inventory data.

Page 1 of 2

Site	Air District	Tier	Number ^a of Speciated VOC samples > 50 ppbC	Number ^b of NO _x samples > 10 ppb	Number of Wind ^b samples	TOG Emissions (tons/day)	NO _x Emissions (tons/day)	Designation ^c	Local or Regional Emissions ^d	Number ^b of TNMOC samples > 50 ppbC	Number ^b of CO samples > 0.15 ppm
BGS	San Joaquin Valley Unified	1	27	103	752	76	53	Urban	Local	191	24
CLO	San Joaquin Valley Unified	1	21	78	750	199	46	Urban	Local		22
FSF	San Joaquin Valley Unified	1	29	92	746	210	49	Urban	Local	246	20
NAT	Sacramento Metro	1	26	85	756	65	53	Rural	Mixed		24
SDP	Sacramento Metro	1	20	65	756	93	67	Urban	Local		19
FLN	Sacramento Metro	2	24	33	569	46	28	Urban	Local		
PLR	San Joaquin Valley Unified	2	25	42	751	63	18	Rural	Regional		
SUN	San Francisco Bay Area	3	30	343 ^e	756	94	37	Rural	Regional		527 ^e
ARV	San Joaquin Valley Unified	3	21	37	750	11	9	Rural	Regional	88	
ELK	Sacramento Metro	3	11	50	751	10	20	Rural	Regional		
SJ4	San Francisco Bay Area	3	6	151		137	85	Urban	Local		32
M29	San Joaquin Valley Unified	3	25	81	748	32	15	Rural	Regional		
BTI	San Francisco Bay Area	3	35	41	623	15	15	Rural	Regional		8
BODB	Northern Sonoma	3	11	NO _y only	756	2	1	Rural	Regional	1	NA
SHA	San Joaquin Valley Unified	3	20	101	752	14	12	Urban	Mixed	239	
TSM	San Joaquin Valley Unified	3	7	89	756	65	25	Urban	Local		18
BAC	San Joaquin Valley Unified	4		86	754	69	49	Urban	Local	49	18
ELM	Ventura	4		64	753	41	19	Rural	Regional	33	8
FSS	San Joaquin Valley Unified	4		59	749	171	41	Rural	Mixed		13
M14	San Joaquin Valley Unified	4		79	756	155	29	Urban	Local		21
ROS	Placer	4		68	644	75	45	Urban	Local		15
S13	Sacramento Metro	4		103	755	79	59	Urban	Local		24
SIM	Ventura	4		109	749	36	20	Urban	Local	28	33
SOH	San Joaquin Valley Unified	4		110	687	61	41	Urban	Local		24
VCS	San Joaquin Valley Unified	4		68	753	81	19	Urban	Local		15

^a Approximately 30-37 samples are expected based on 30 regular samples (3-hr duration, once every third day) and special episode predicted samples.

^b Approximately 750 samples are expected based on hourly measurements.

^c Urban and rural designations are from site designations in the CCOS database.

^d Local, mixed, or regional emissions designations were made using visual site inspections from Google™ Earth. Local sites had clear emissions sources near the monitor; regional sites had no obvious local emissions sources.

^e NO_x and CO samples at the Sunol site were one-minutes duration and represented fewer than 10 distinct hours.

Table 1. Summary of measurement sites collecting data considered for comparison with emission inventory data.

Site	Air District	Tier	Number ^a of Speciated VOC samples > 50 ppbC	Number ^b of NO _x samples > 10 ppb	Number of Wind ^b samples	TOG Emissions (tons/day)	NO _x Emissions (tons/day)	Designation ^c	Local or Regional Emissions ^d	Number ^b of TNMOC samples > 50 ppbC	Number ^b of CO samples > 0.15 ppm
CHM	Butte	5		65	756	13	9	Urban	Local		20
^e DVP	Monterey Bay Unified	5		18	756	37	5	Rural	Regional		6
DVS	Yolo Solano	5		58	739	13	15	Rural	Mixed		6
FSD	San Joaquin Valley Unified	5		93		188	44	Urban	Local		21
GNF	Santa Barbara	5		45	691	34	13	Urban	Local		11
LOM	Santa Barbara	5		35	748	14	4	Urban	Local		14
LWP	Antelope Valley	5		91	755	21	14	Urban	Local		25
SBC	Santa Barbara	5		75	756	32	12	Urban	Local		22
SLM	San Luis Obispo	5		57	756	17	7	Urban	Local		13
SNH	Sacramento Metro	5		58		92	63	Urban	Local		20
YAS	Feather River	5		72	683	17	15	Urban	Mixed		15

^a Approximately 30-37 samples are expected based on 30 regular samples (3-hr duration, once every third day) and special episode predicted samples.

^b Approximately 750 samples are expected based on hourly measurements.

^c Urban and rural designations are from site designations in the CCOS database.

^d Local, mixed, or regional emissions designations were made using visual site inspections from Google™ Earth. Local sites had clear emissions sources near the monitor; regional sites had no obvious local emissions sources.

^e NO_x and CO samples at the Sunol site were one-minutes duration and represented fewer than 10 distinct hours.

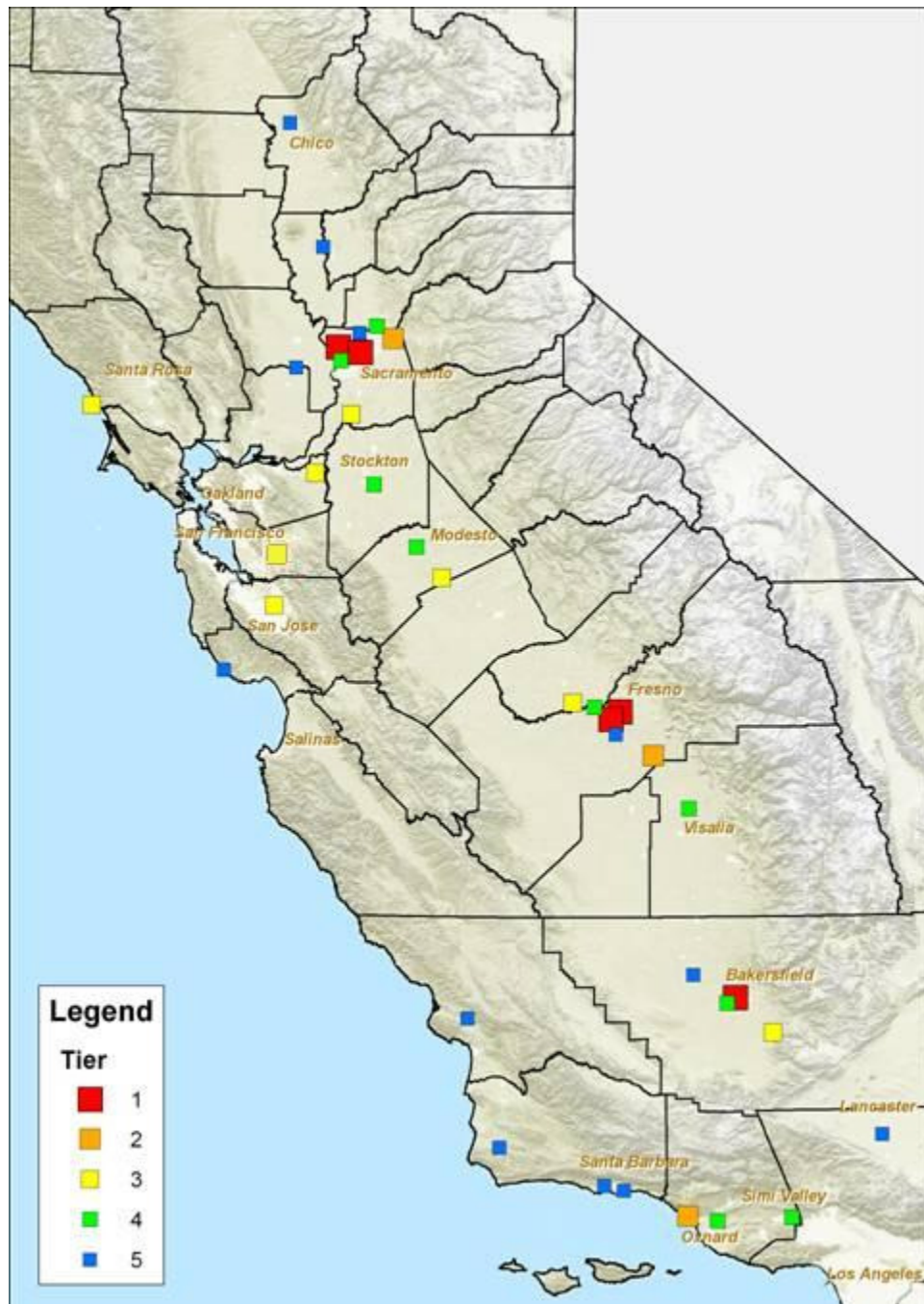


Figure 1. Map of sites and Tier designations. Tier 1 sites are the most suitable sites for emission inventory reconciliation; Tier 5 sites are the least suitable.

Table 2. Available air quality data (July, August, September 2000).

Page 1 of 2

Site	Tier	Total Count ^a	7/1/2000	7/2/2000	7/3/2000	7/4/2000	7/5/2000	7/6/2000	7/7/2000	7/8/2000	7/9/2000	7/10/2000	7/11/2000	7/12/2000	7/13/2000	7/14/2000	7/15/2000	7/16/2000	7/17/2000	7/18/2000	7/19/2000	7/20/2000	7/21/2000	7/22/2000	7/23/2000	7/24/2000	7/25/2000	7/26/2000	7/27/2000	7/28/2000	7/29/2000	7/30/2000	7/31/2000	
FSF	1	518	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
BGS	1	280		X			X			X			X			X			X			X			X			X			X			
NAT	1	27		X									X			X			X			X			X			X			X			
CLO	1	22					X			X			X			X			X									X				X		
SDP	1	21																																
FLN	2	27		X			X			X			X			X						X			X			X			X			
PLR	2	27		X			X			X			X			X			X			X			X			X			X			
ARV	3	196		X			X			X			X			X			X			X			X			X			X			
M29	3	26		X												X			X						X			X			X			
ELK	3	11					X																											

Site	Tier	Total Count ^a	8/1/2000	8/2/2000	8/3/2000	8/4/2000	8/5/2000	8/6/2000	8/7/2000	8/8/2000	8/9/2000	8/10/2000	8/11/2000	8/12/2000	8/13/2000	8/14/2000	8/15/2000	8/16/2000	8/17/2000	8/18/2000	8/19/2000	8/20/2000	8/21/2000	8/22/2000	8/23/2000	8/24/2000	8/25/2000	8/26/2000	8/27/2000	8/28/2000	8/29/2000	8/30/2000	8/31/2000
FSF	1	518	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X		X	X	
BGS	1	280	X			X			X			X			X			X			X	X	X	X	X	X	X	X	X	X	X	X	
NAT	1	27	X			X			X			X			X			X			X			X								X	
CLO	1	22				X			X			X			X			X			X						X			X		X	
SDP	1	21	X			X			X			X			X			X			X			X								X	
FLN	2	27	X			X						X			X			X			X			X								X	
PLR	2	27	X			X			X			X			X			X						X				X				X	
ARV	3	196										X			X			X			X			X			X	X	X	X	X	X	
M29	3	26	X			X			X			X			X			X			X			X			X			X			X
ELK	3	11															X							X									X

^a Includes samples of 1-hr and 3-hr durations.

Table 2. Available air quality data (July, August, September 2000).

Page 2 of 2

Site	Tier	Total Count ^a	9/1/2000	9/2/2000	9/3/2000	9/4/2000	9/5/2000	9/6/2000	9/7/2000	9/8/2000	9/9/2000	9/10/2000	9/11/2000	9/12/2000	9/13/2000	9/14/2000	9/15/2000	9/16/2000	9/17/2000	9/18/2000	9/19/2000	9/20/2000	9/21/2000	9/22/2000	9/23/2000	9/24/2000	9/25/2000	9/26/2000	9/27/2000	9/28/2000	9/29/2000	9/30/2000
FSF	1	518	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
BGS	1	280	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
NAT	1	27			X			X			X			X			X		X	X	X	X										
CLO	1	22			X			X			X			X					X										X			X
SDP	1	21			X			X			X			X			X		X	X	X	X	X									
FLN	2	27			X			X			X			X			X		X	X	X	X	X									
PLR	2	27			X									X					X			X				X			X			X
ARV	3	196	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
M29	3	26						X			X			X			X		X			X				X			X			X
ELK	3	11						X			X			X			X		X	X	X											

^a Includes samples of 1-hr and 3-hr durations.

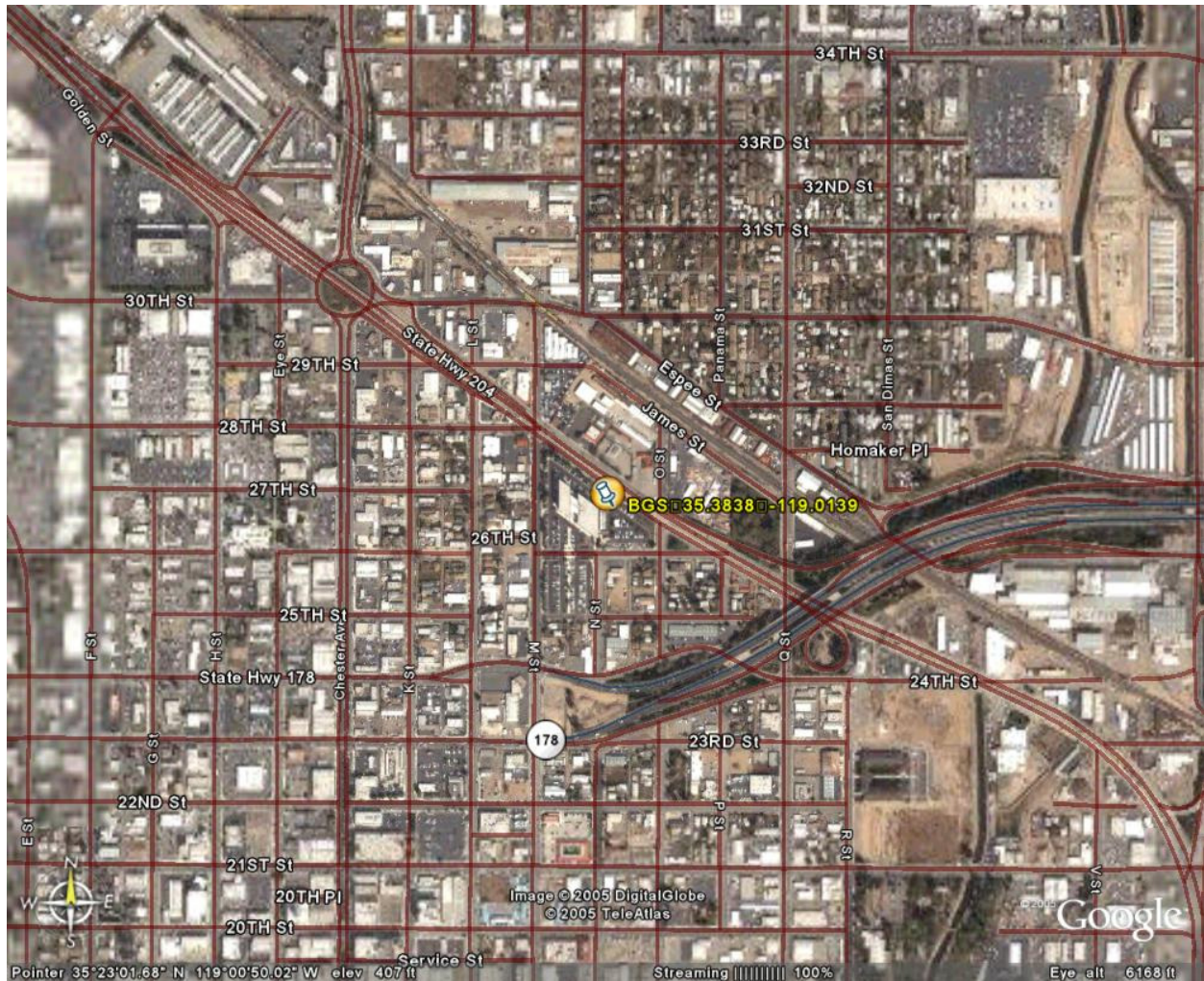


Figure 2. Bakersfield Station (1128 Golden State) (BGS), 2-km width.

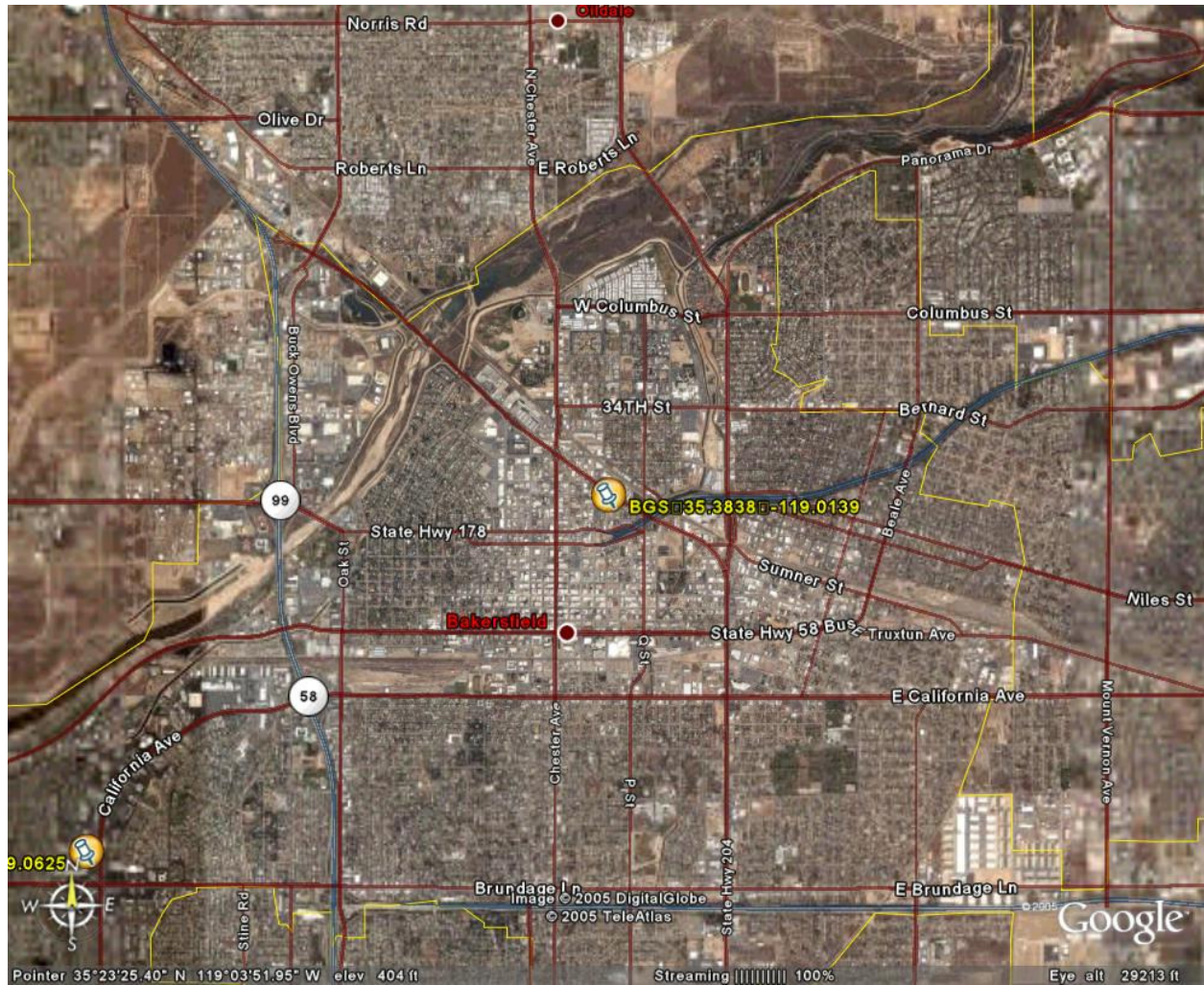


Figure 3. Bakersfield Station (1128 Golden State) (BGS), 10-km width.



Figure 4. Clovis Station (908 N Villa Ave.) (CLO), 2-km width.

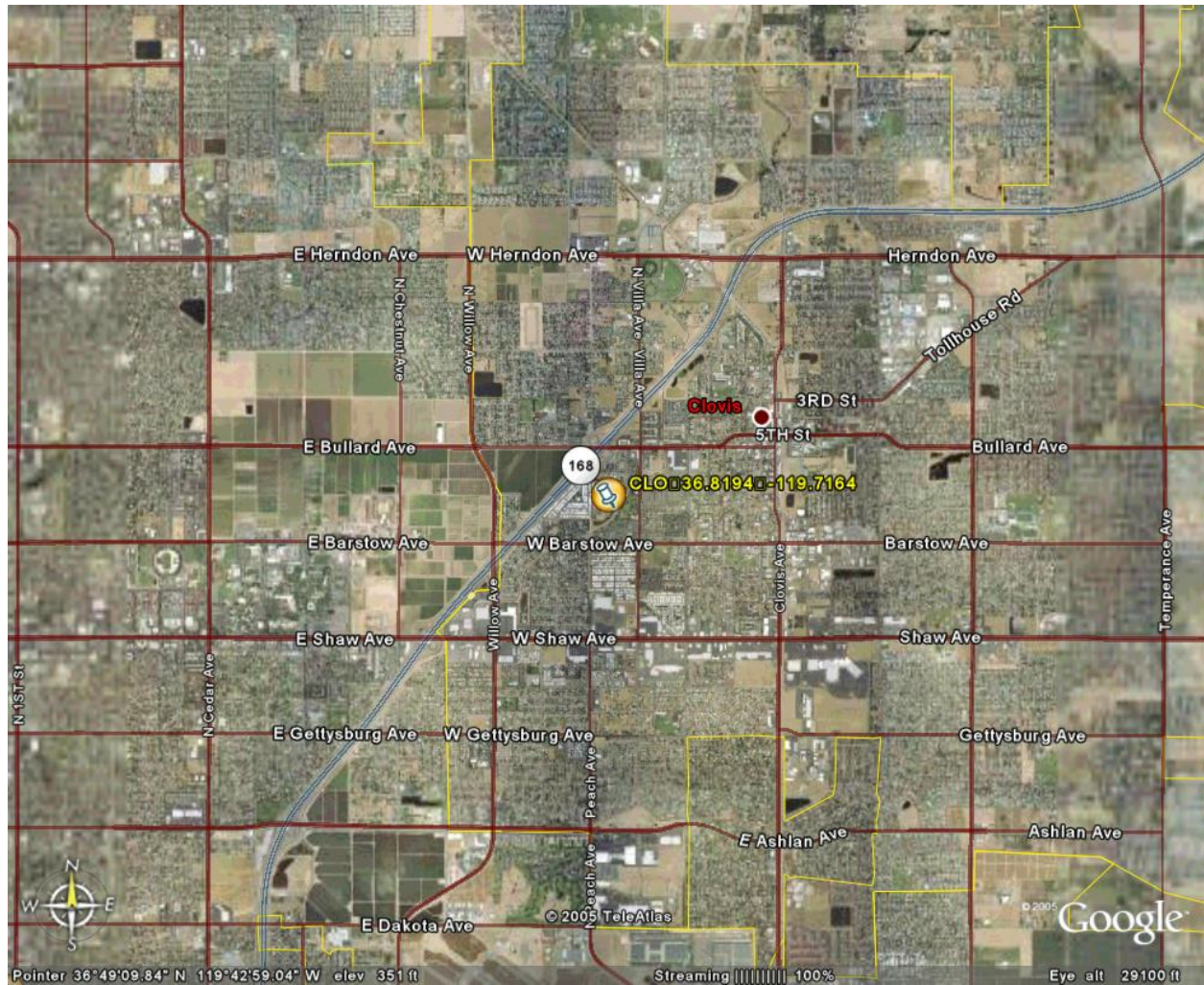


Figure 5. Clovis Station (908 N Villa Ave.) (CLO), 10-km width.

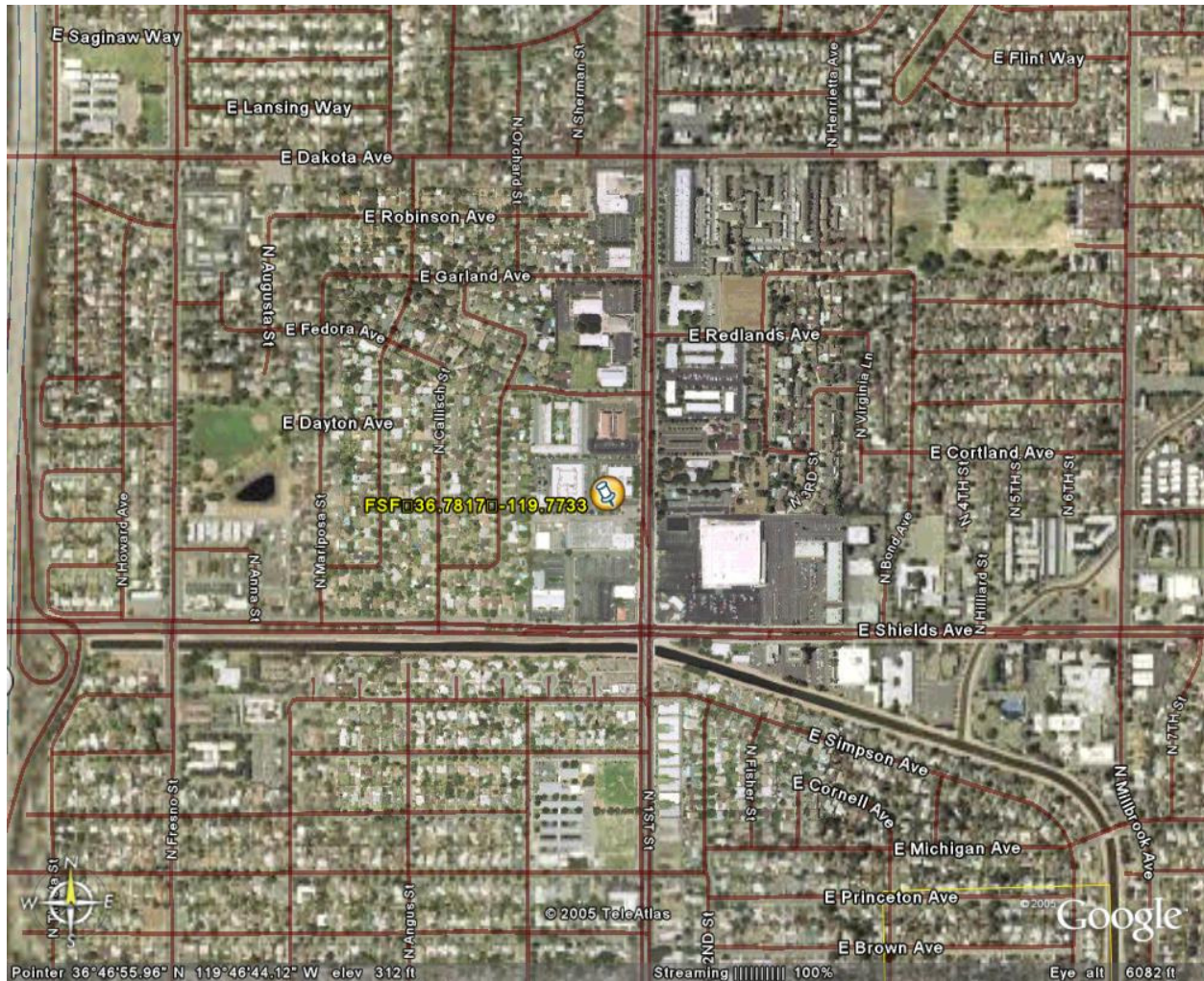


Figure 6. Fresno Station (3425 First St.) (FSF), 2-km width.

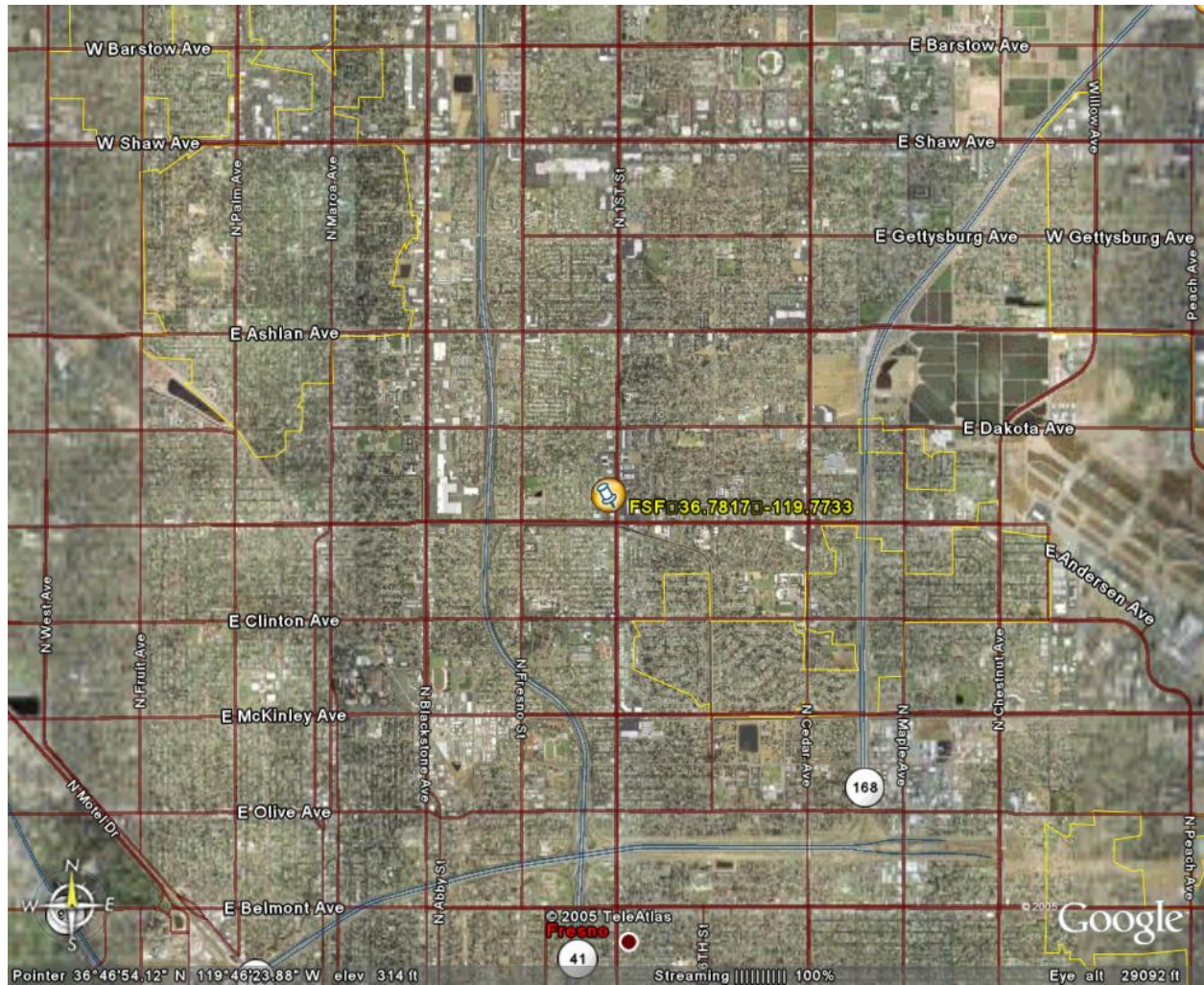


Figure 7. Fresno Station (3425 First St.) (FSF), 10-km width.



Figure 8. Sacramento/Natomas Stn (3801 Airport Rd.) (NAT), 2-km width.

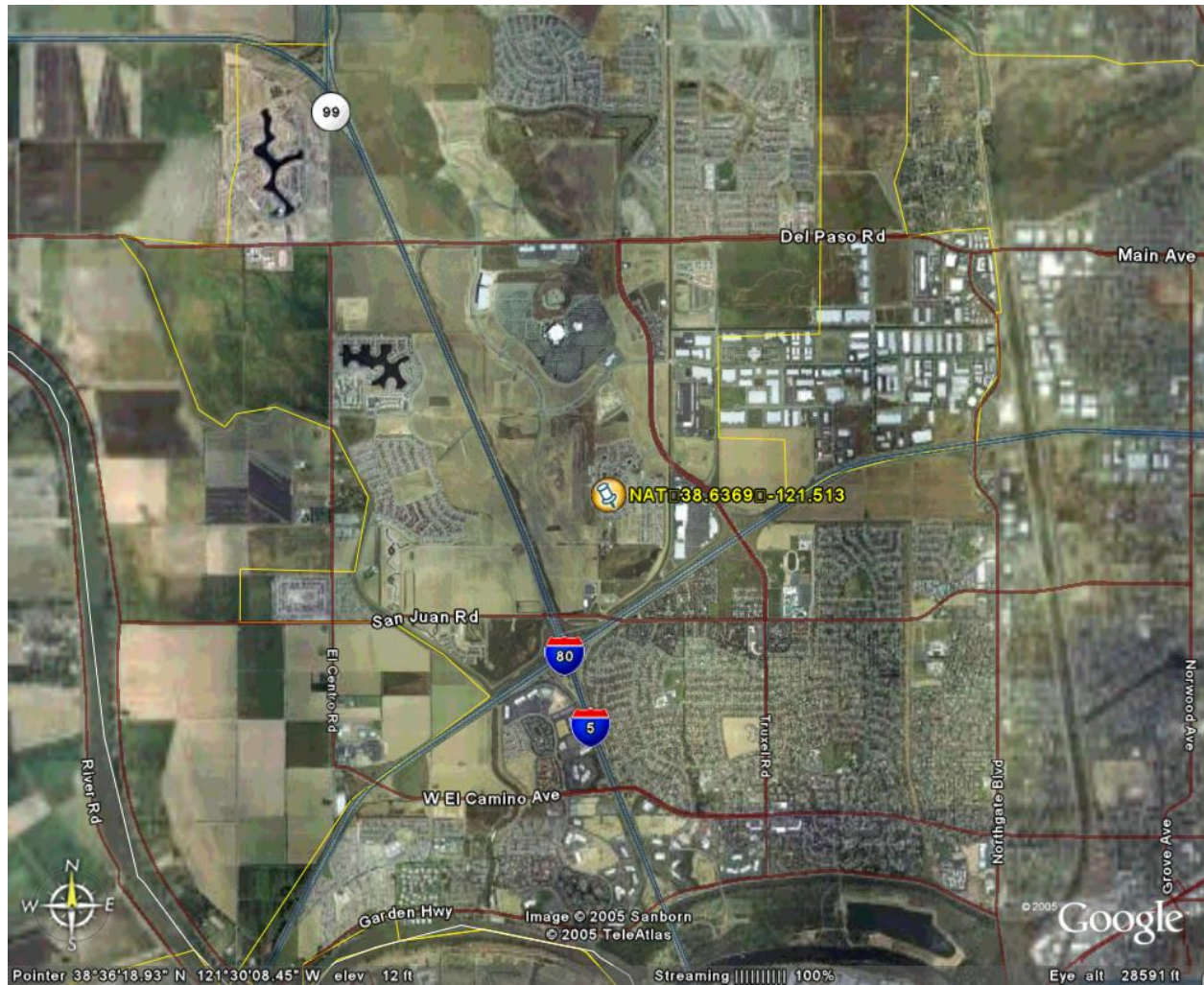


Figure 9. Sacramento/Natomas Stn (3801 Airport Rd.) (NAT), 10-km width.

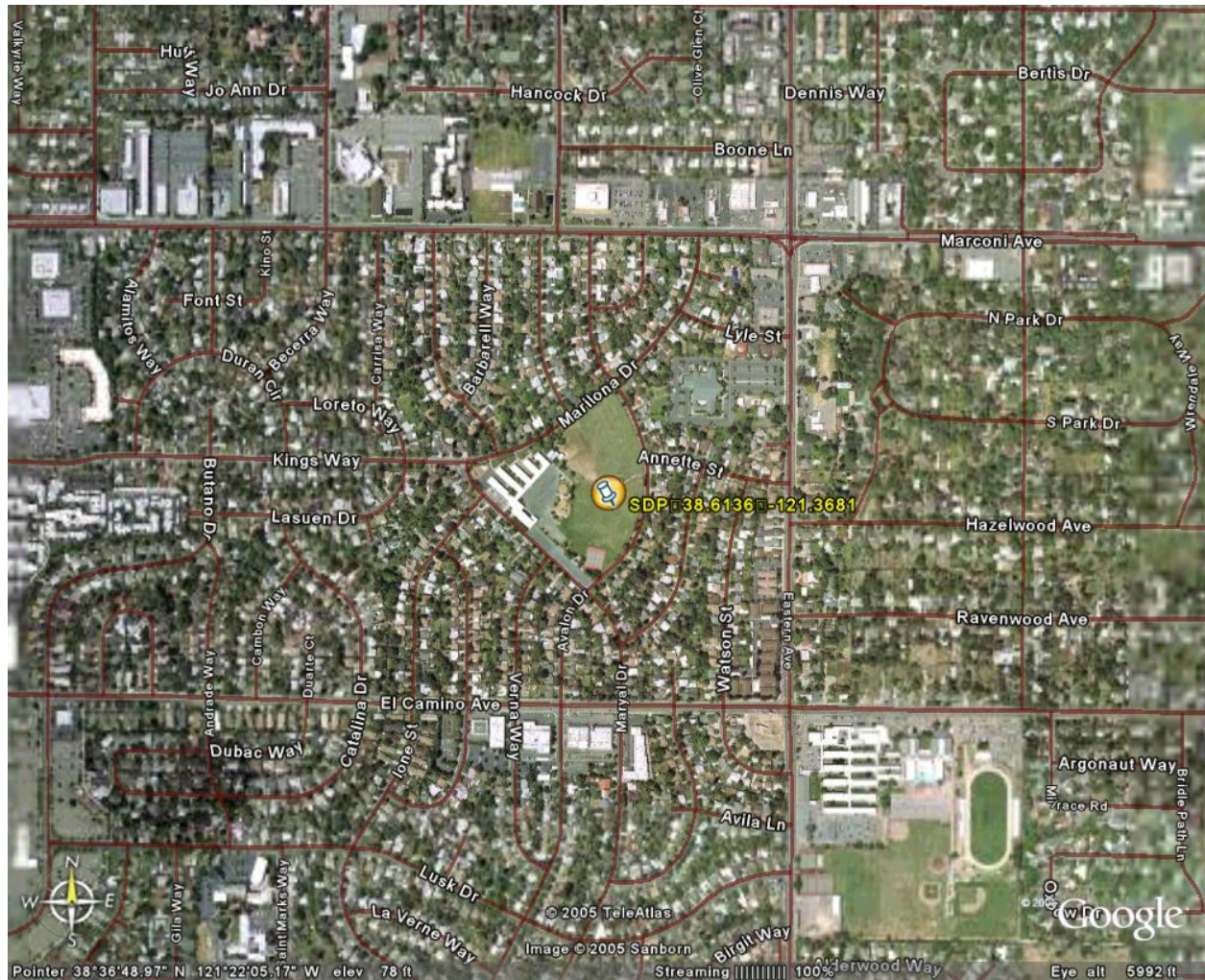


Figure 10. Sacramento Station (Del Paso Manor) (SDP), 2-km width.

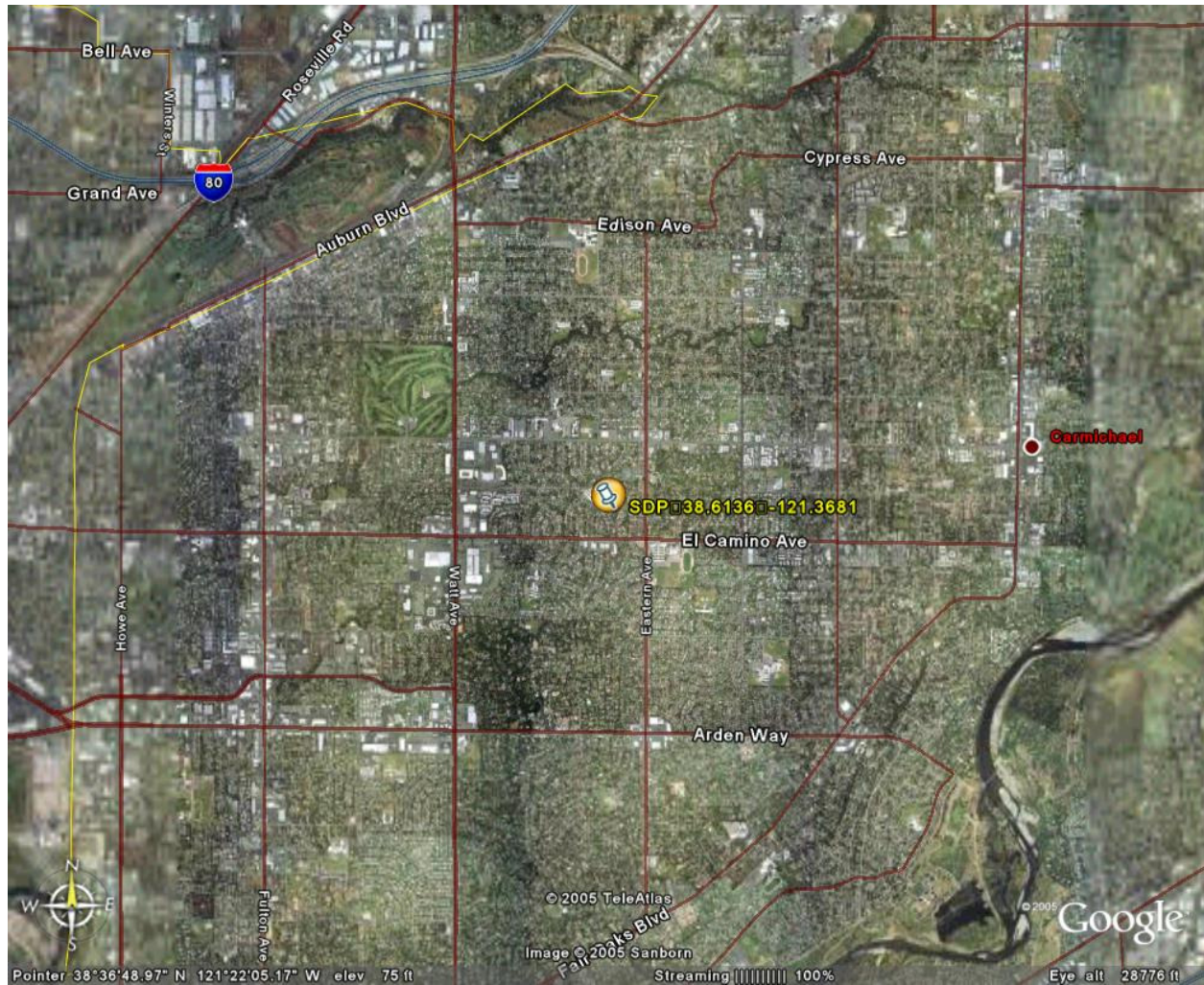


Figure 11. Sacramento Station (Del Paso Manor) (SDP), 10-km width.

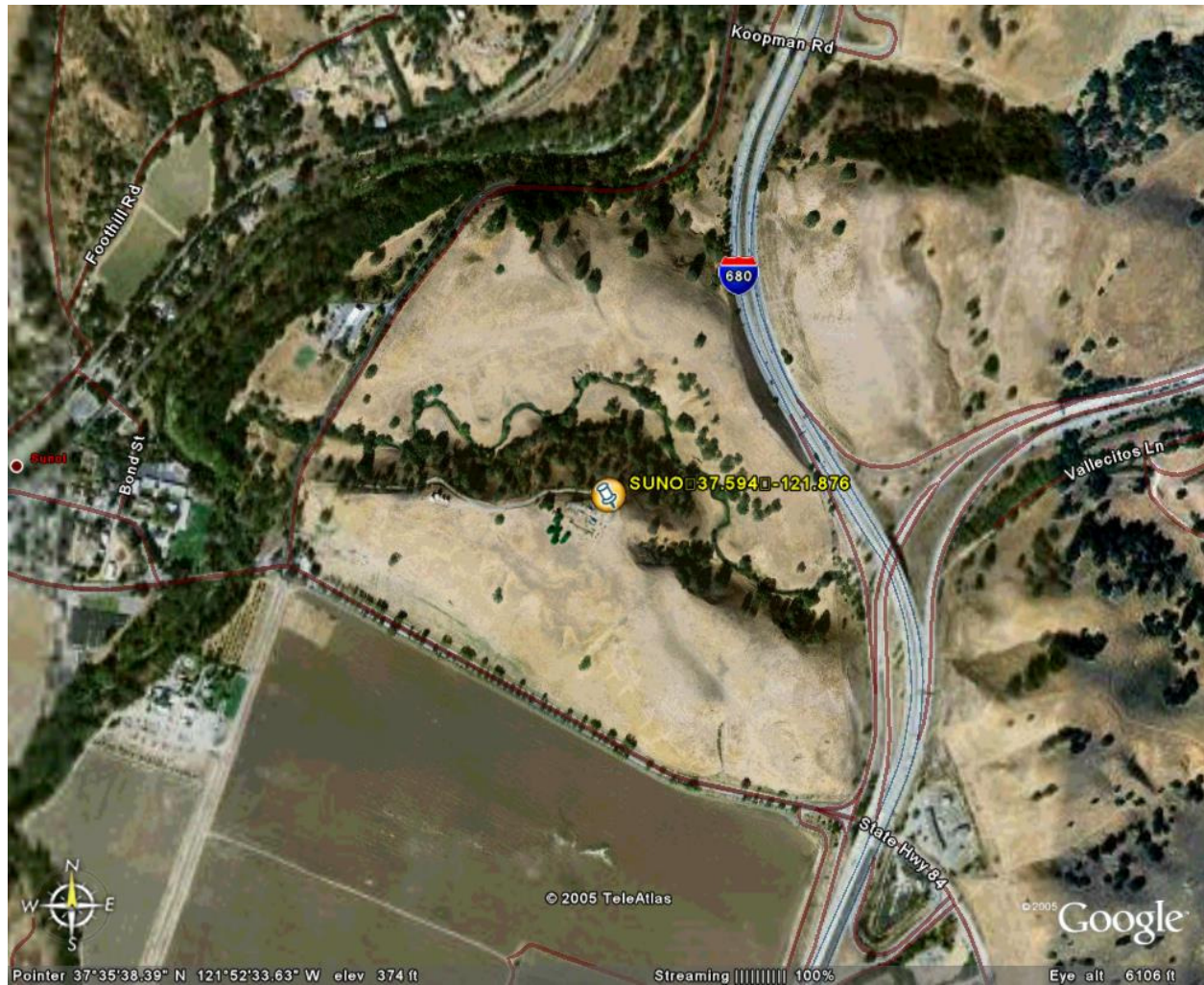


Figure 12. Sunol Station (SUN), 2-km width.



Figure 13. Sunol Station (SUN), 10-km width.



Figure 14. Folsom Station (Natoma St.) (FLN), 2-km width.

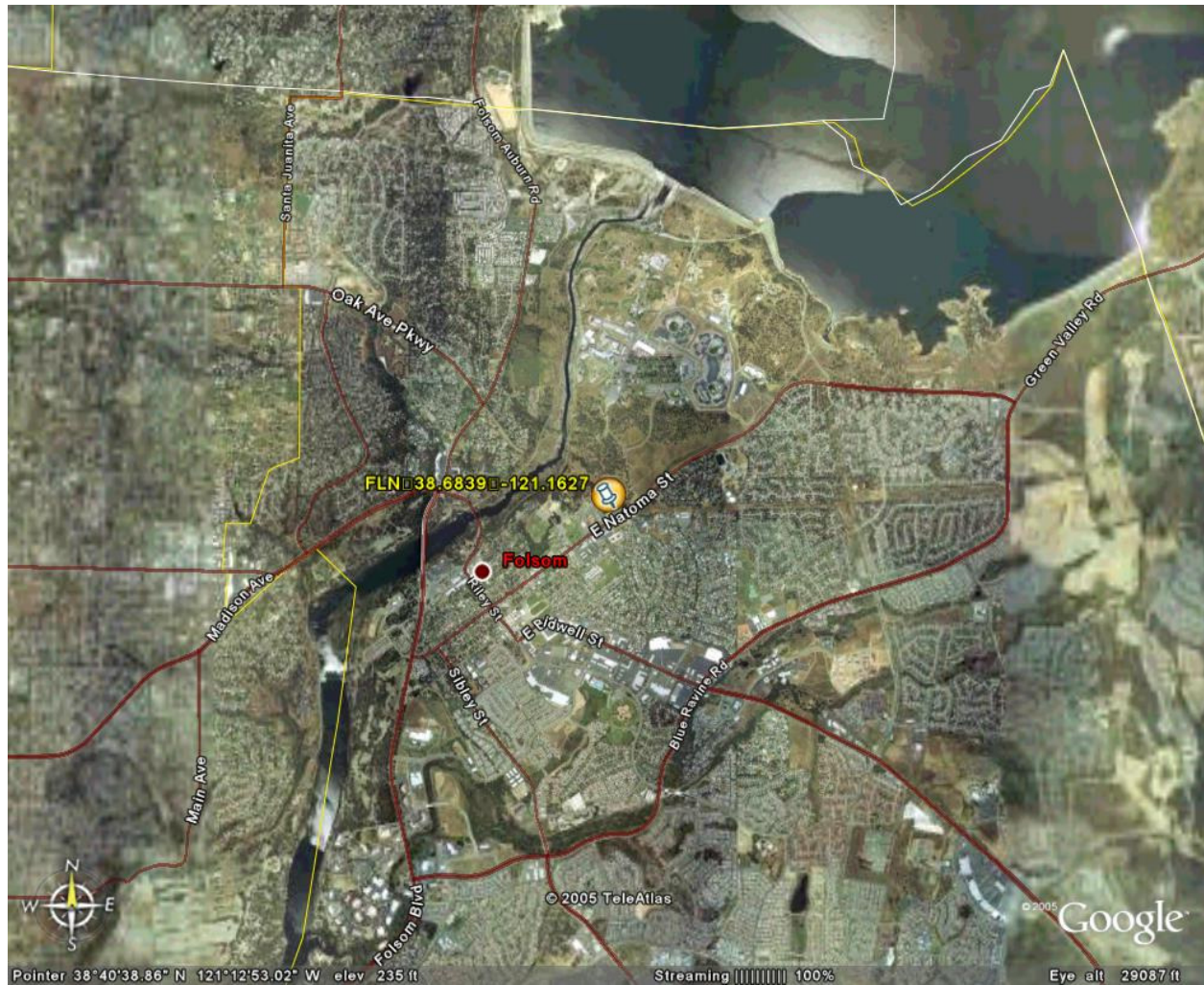


Figure 15. Folsom Station (Natoma St.) (FLN), 10-km width.



Figure 16. Parlier Station (PLR), 2-km width.

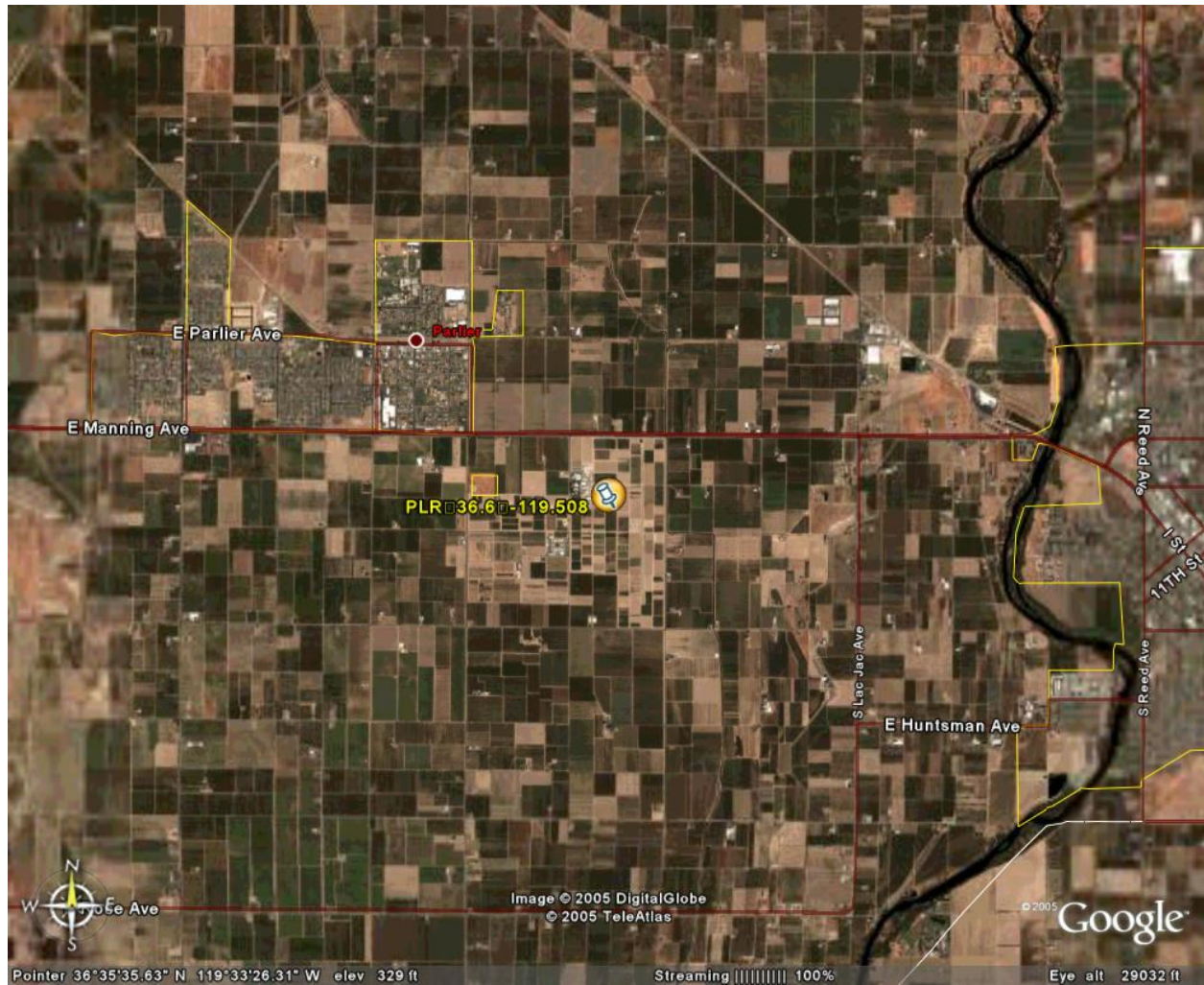


Figure 17. Parlier Station (PLR), 10-km width.

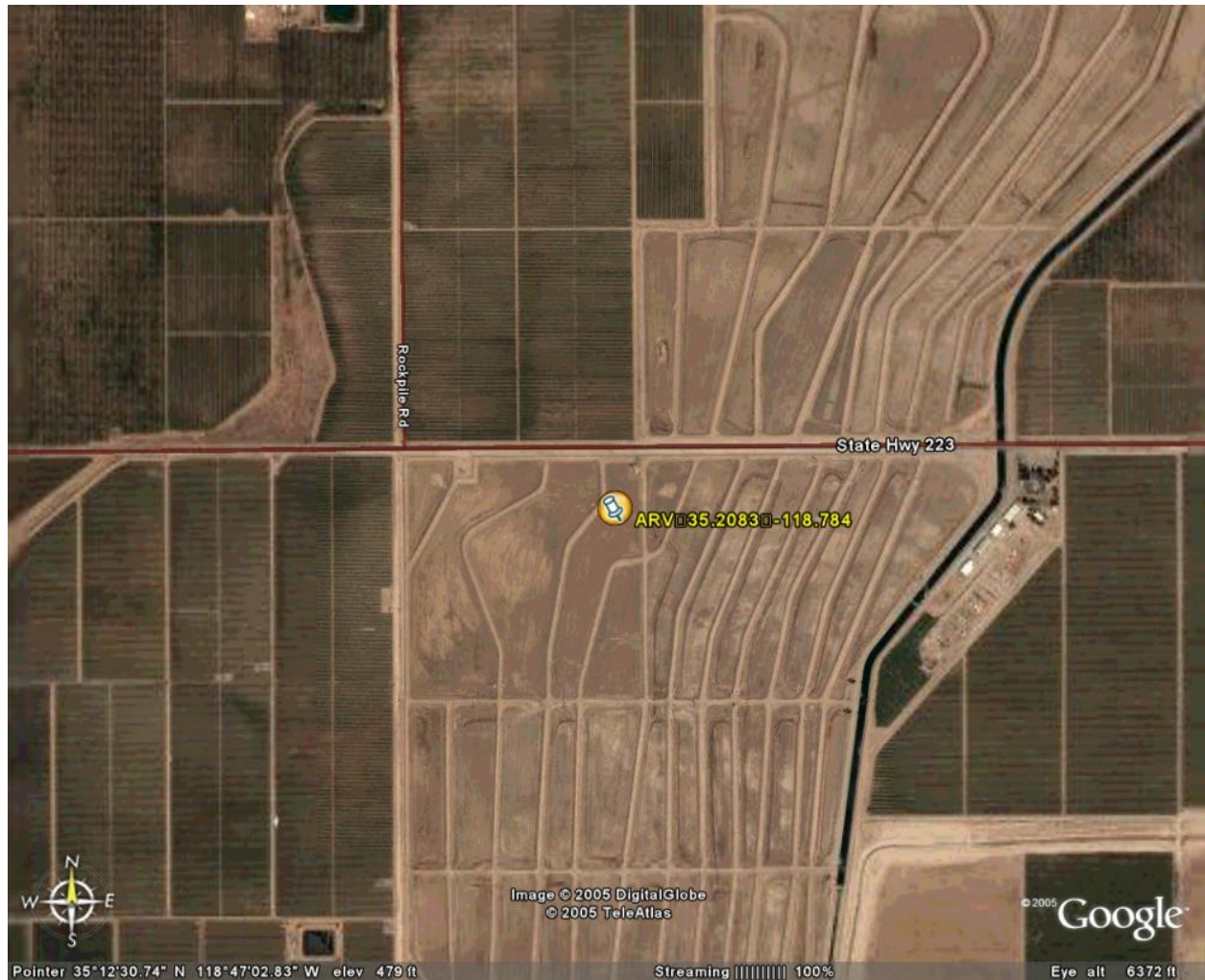


Figure 18. Arvin Station (ARV), 2-km width.

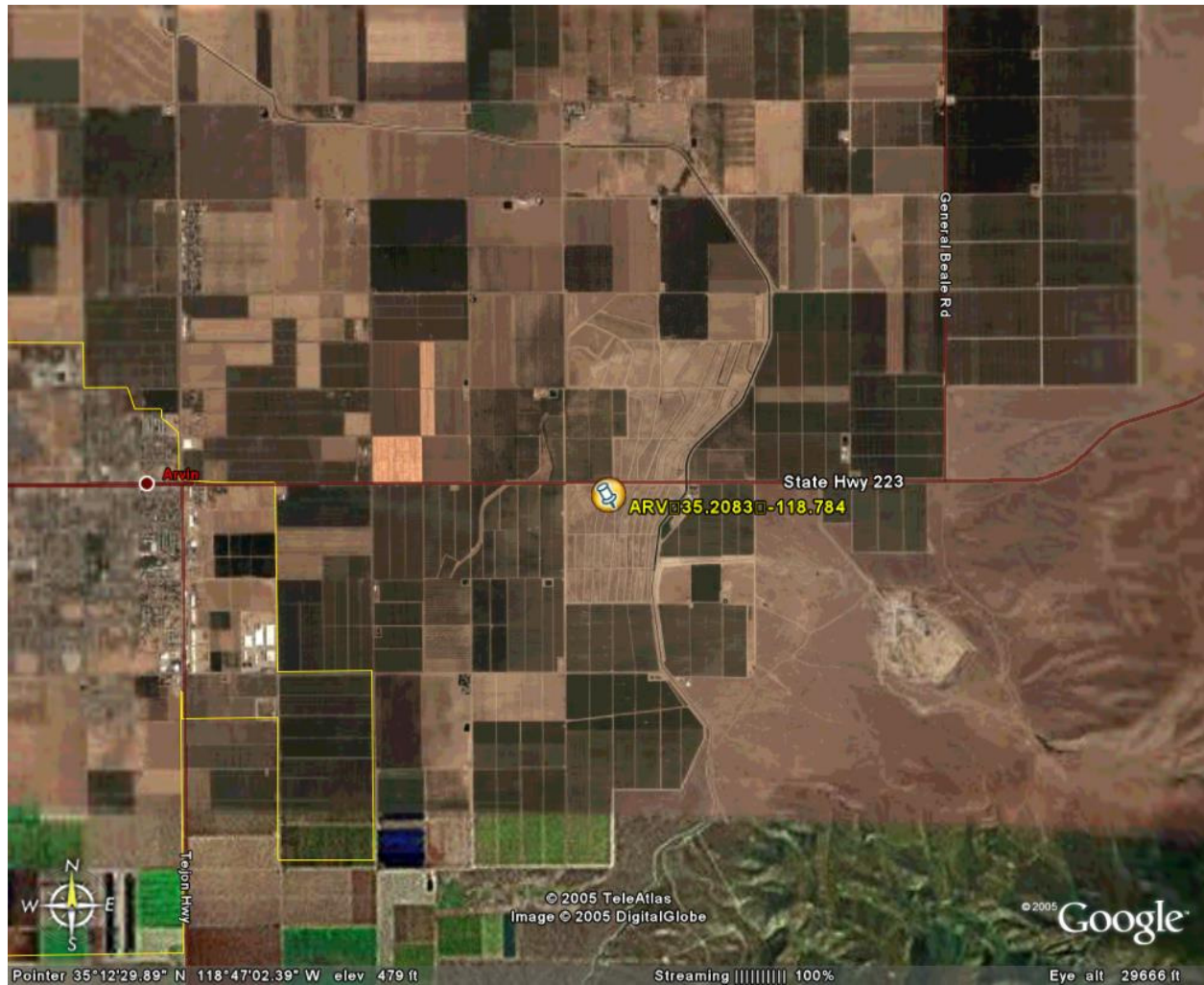


Figure 19. Arvin Station (ARV), 10-km width.



Figure 20. Elk Grove Station (Bruceville Rd.) (ELK), 2-km width.

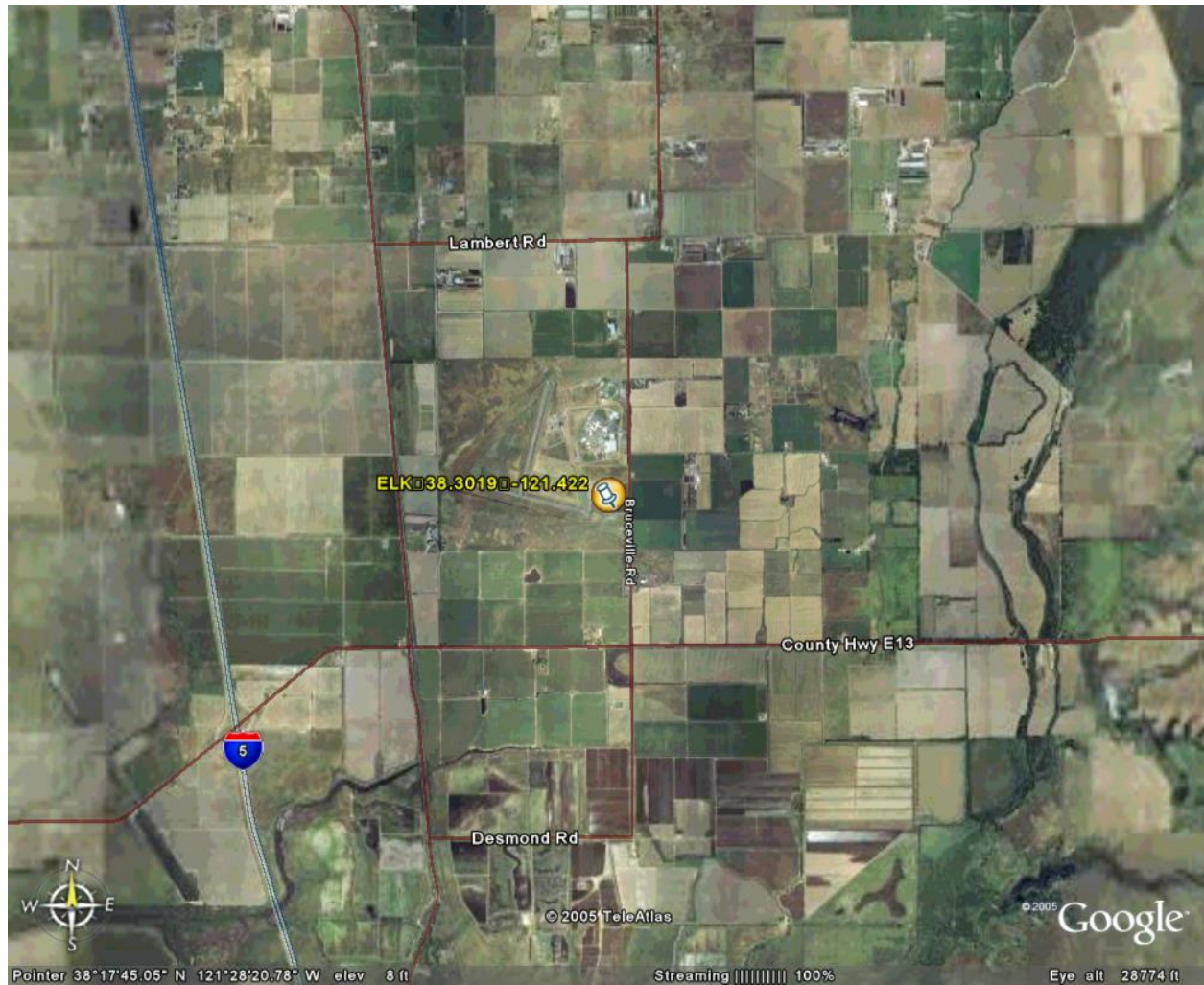


Figure 21. Elk Grove Station (Bruceville Rd.) (ELK), 10-km width.

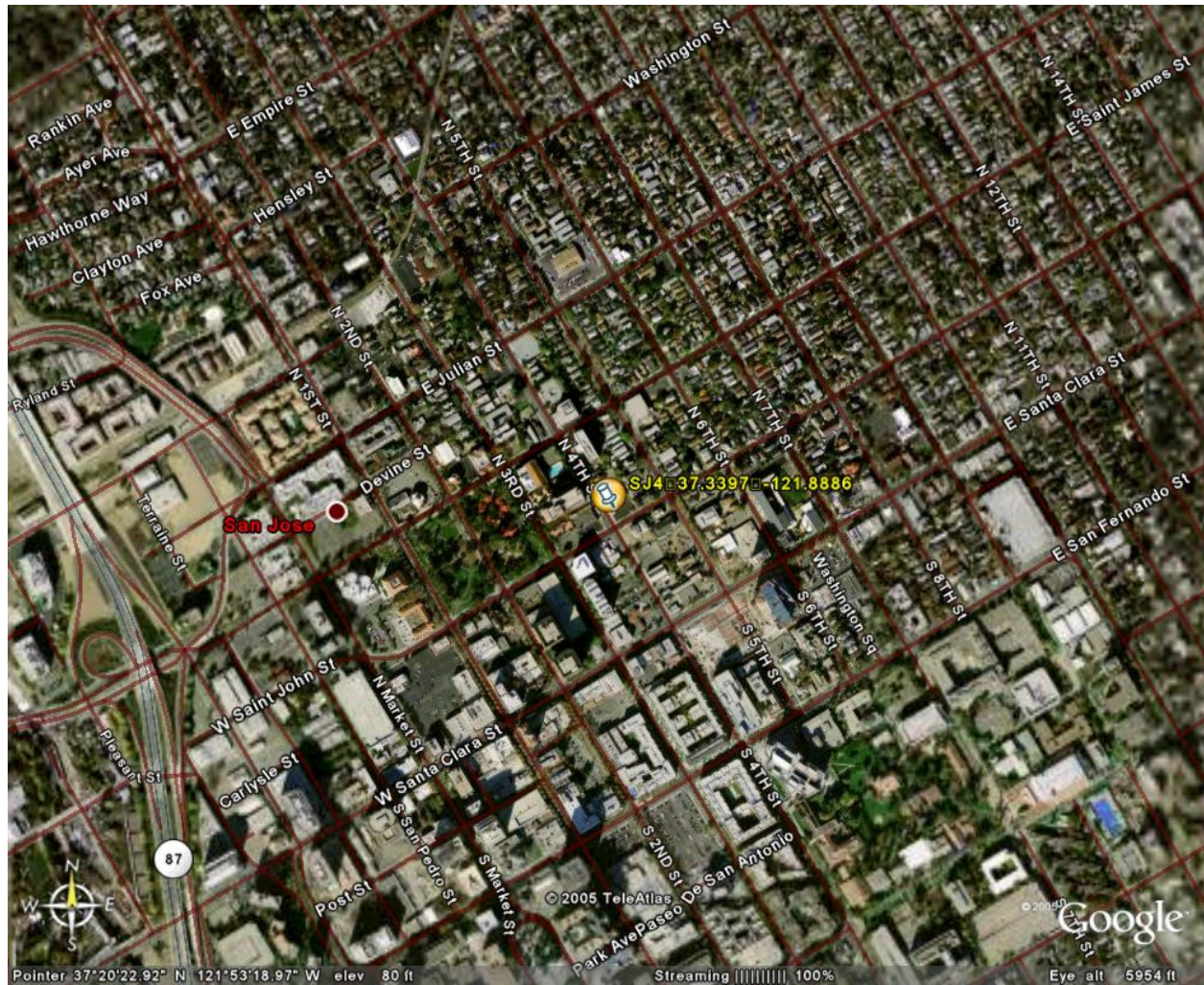


Figure 22. San Jose 4th Street Station (SJ4), 2-km width.

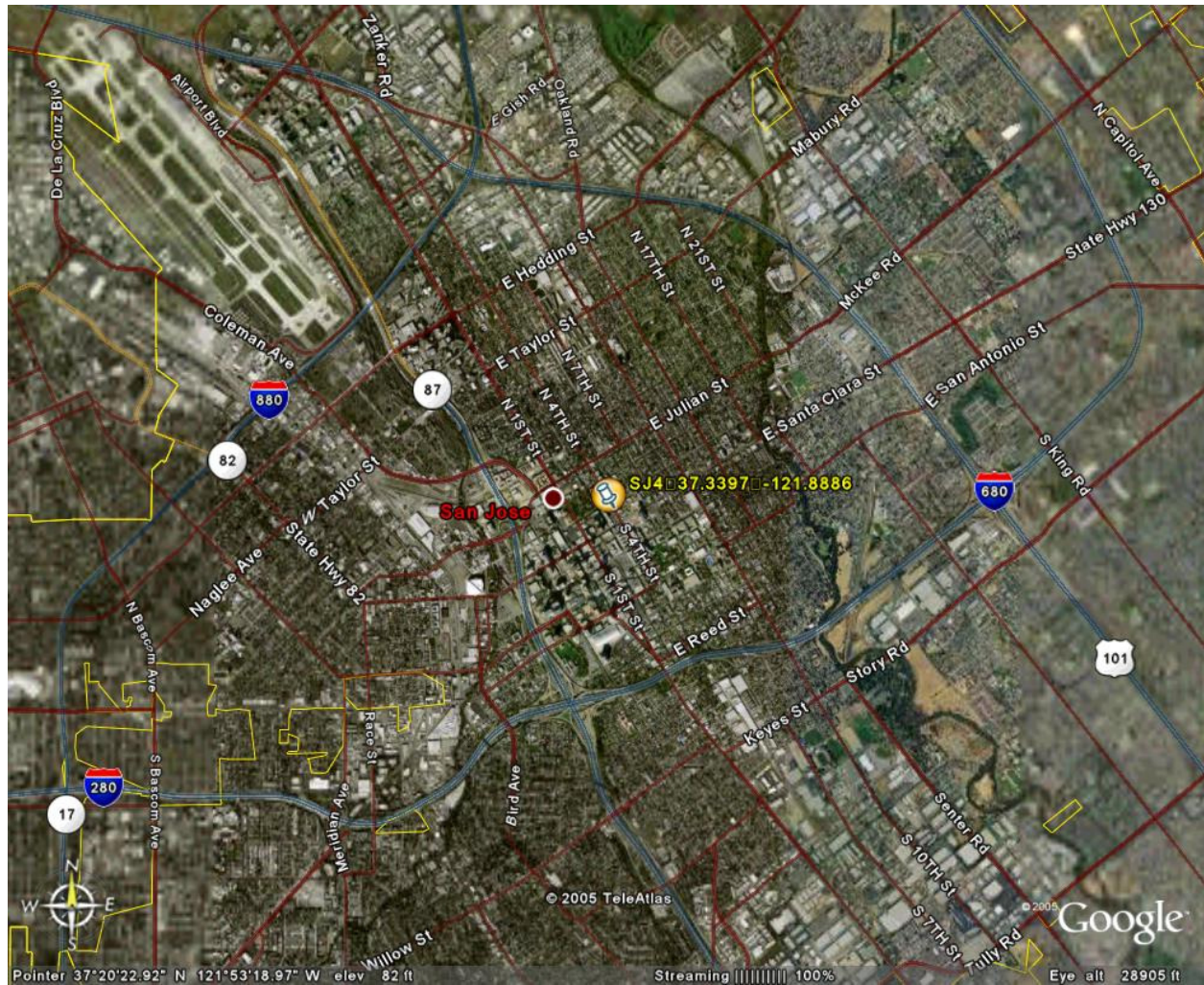


Figure 23. San Jose 4th Street Station (SJ4), 10-km width.

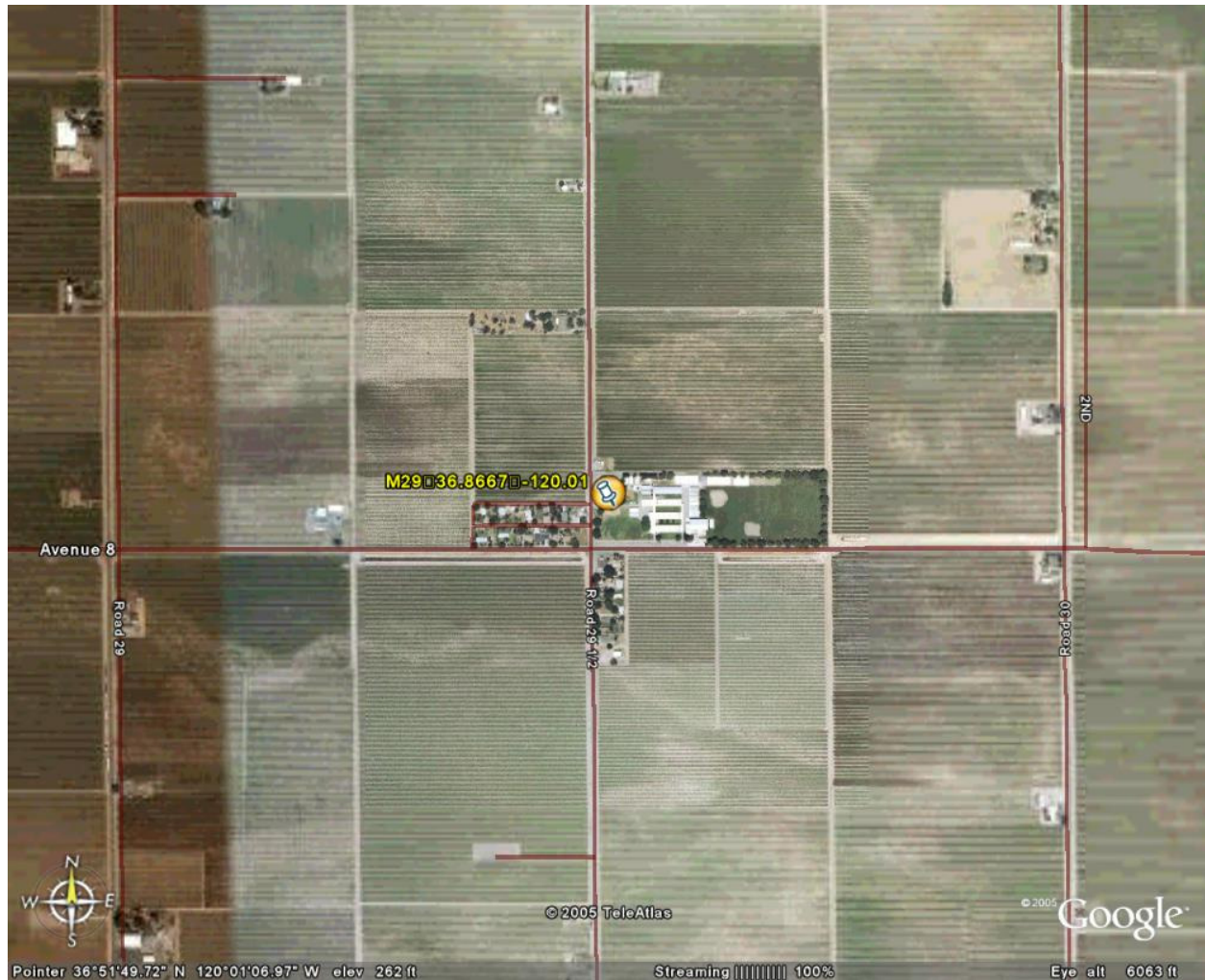


Figure 24. Madera Station (29 1/2 No. of Ave 8) (M29), 2-km width.

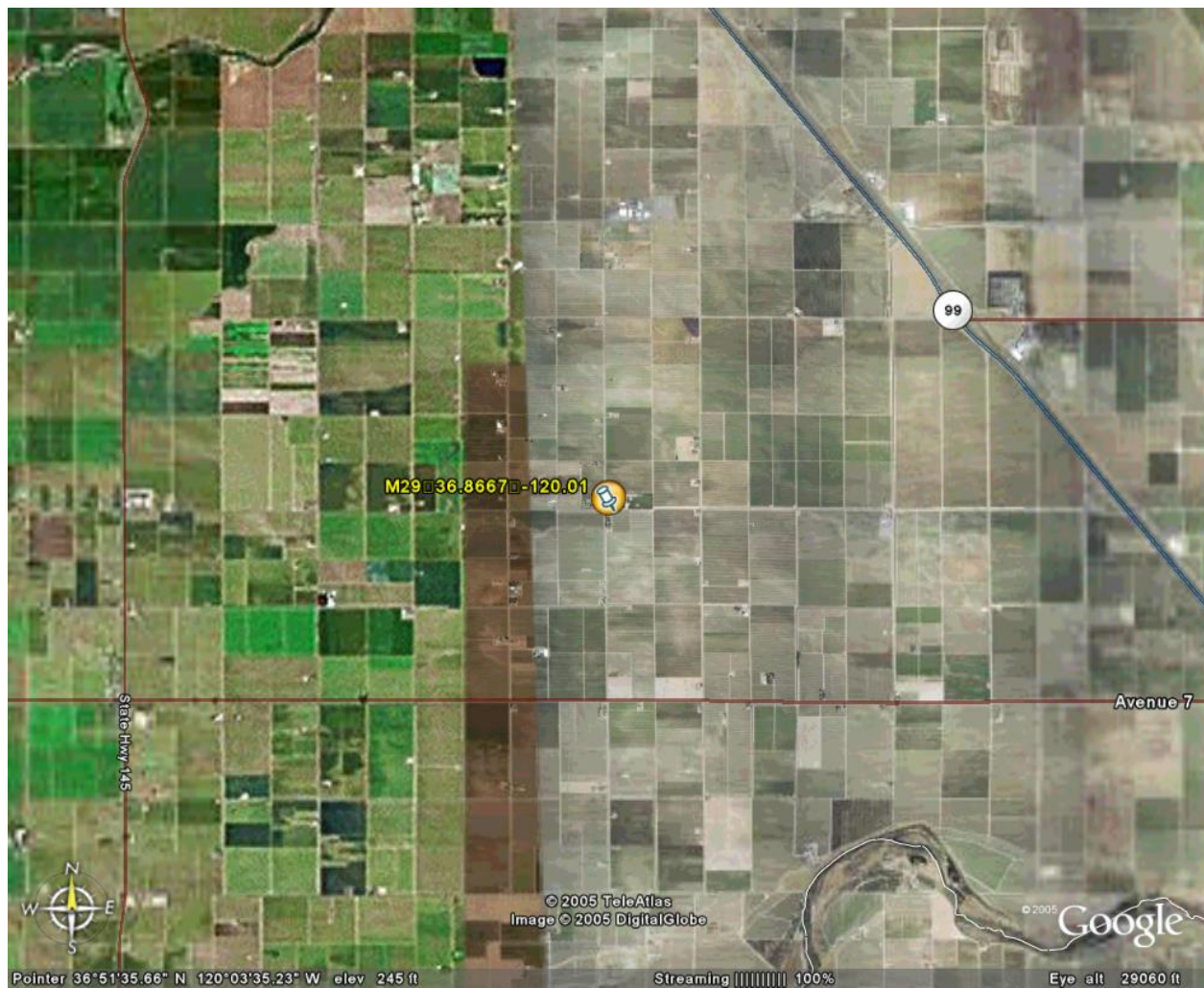


Figure 25. Madera Station (29 1/2 No. of Ave 8) (M29), 10-km width.



Figure 26. Bethel Island Station (BTI), 2-km width.

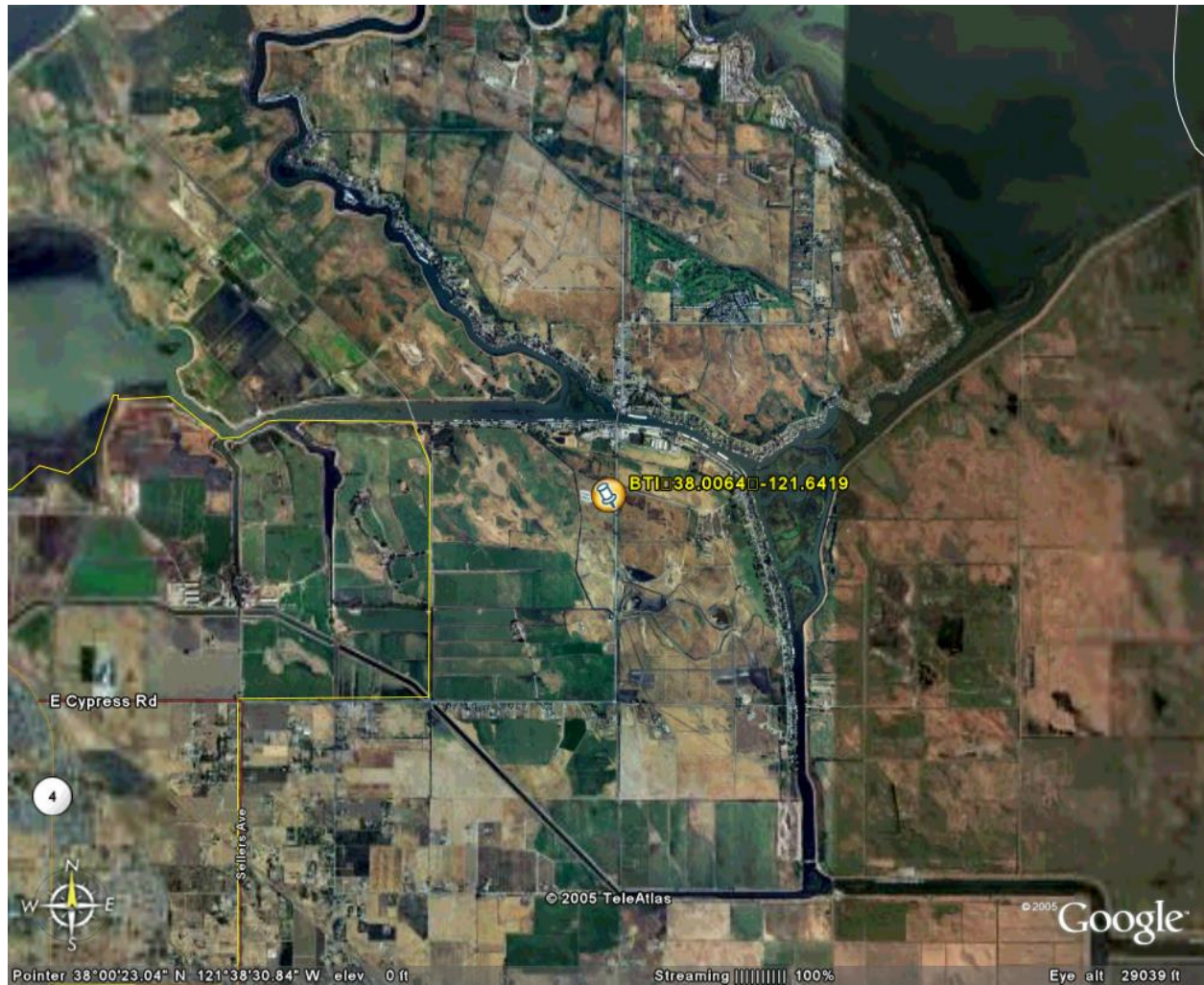


Figure 27. Bethel Island Station (BTI), 10-km width.

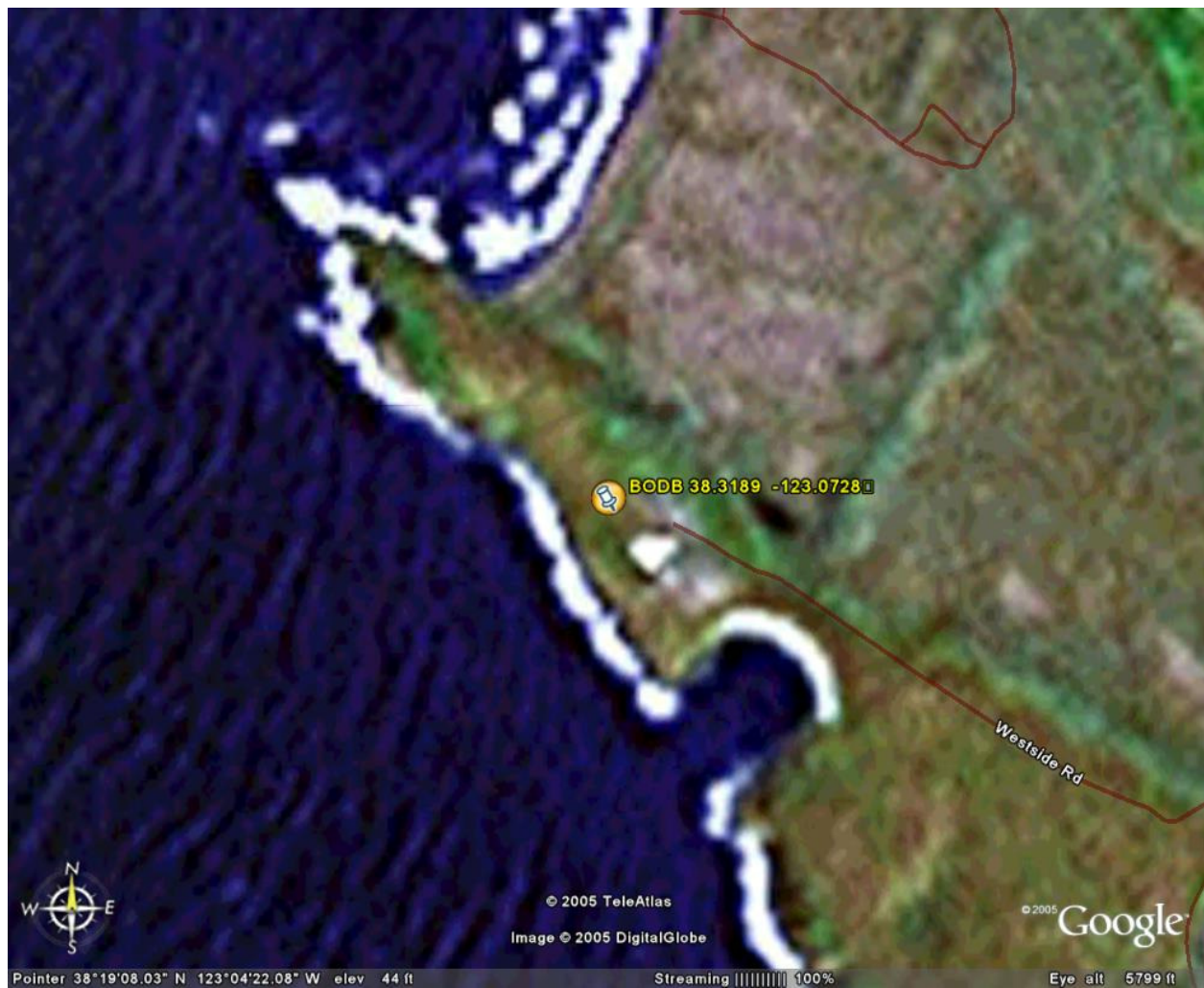


Figure 28. Bodega Bay Station (BODB), 2-km width.

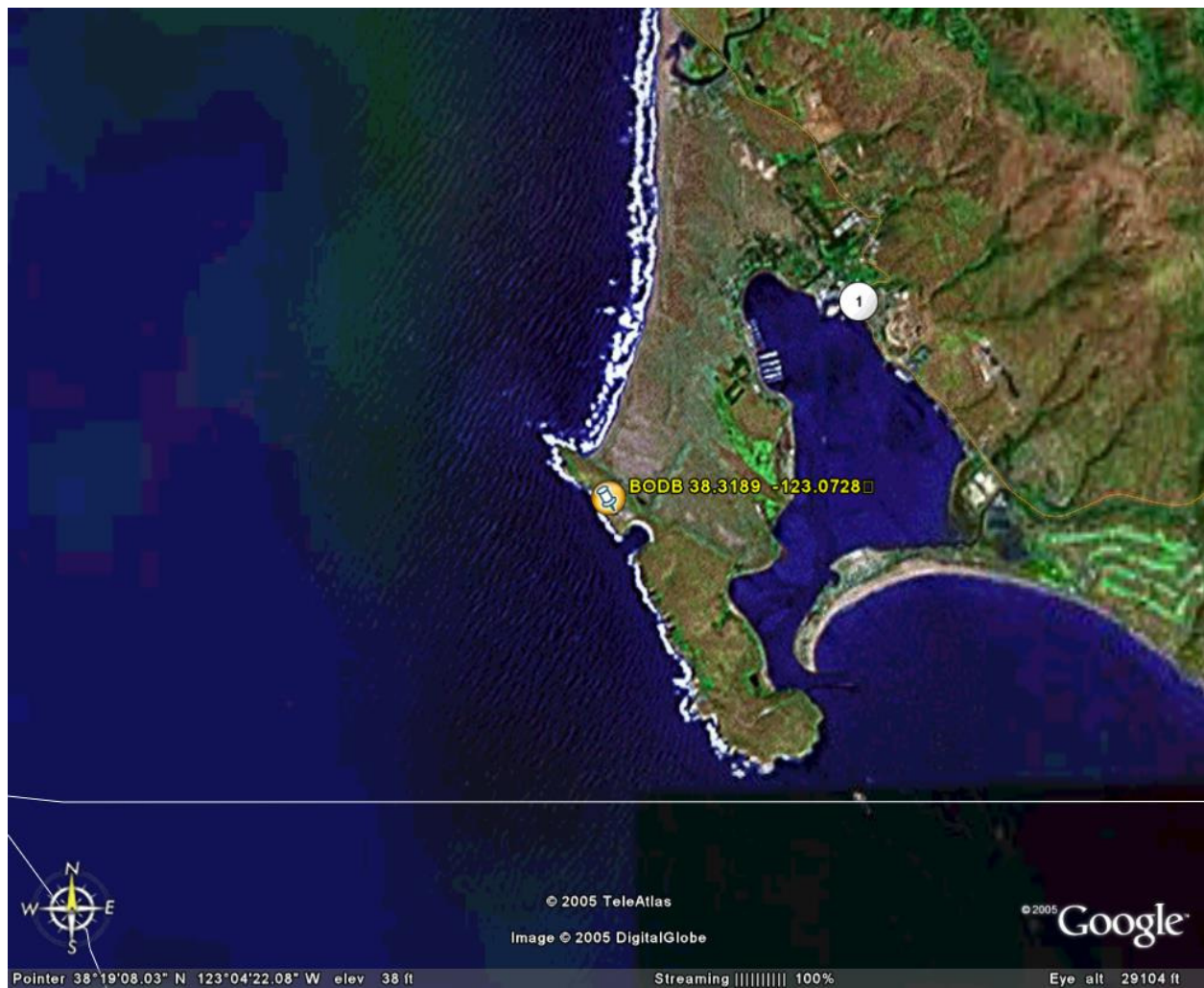


Figure 29. Bodega Bay Station (BODB), 10-km width.

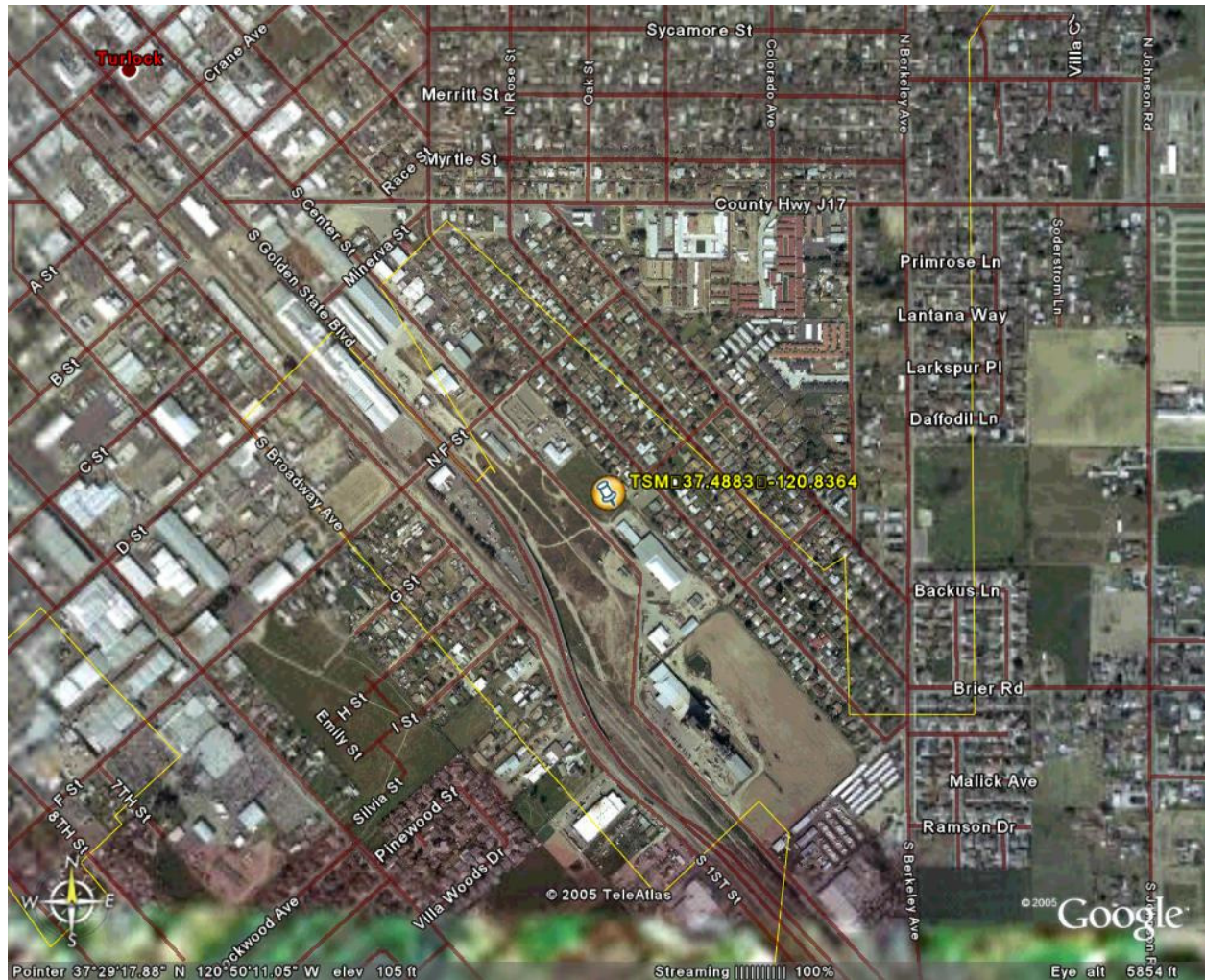


Figure 30. Turlock Station (900 S Minaret) (TSM), 2-km width.

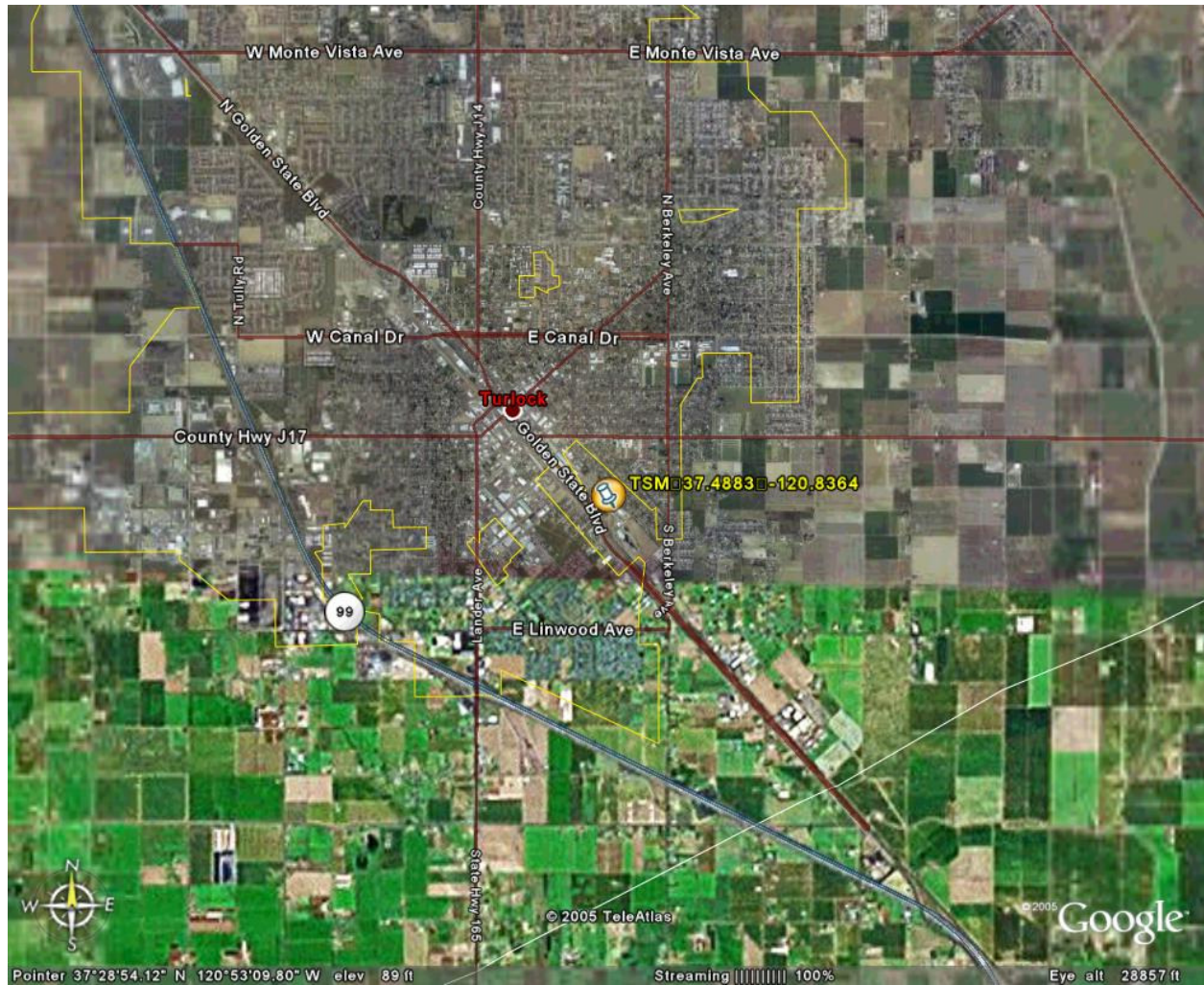


Figure 31. Turlock Station (900 S Minaret) (TSM), 10-km width.

APPENDIX B

SPECIATION PROFILE RECOMMENDATIONS DECEMBER 15, 2005

TECHNICAL MEMORANDUM

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December 15, 2005

STI-905044.03-2860

TO: Dr. Patricia Velasco, California Air Resources Board

FROM: Lyle R. Chinkin, Senior Vice President, and Stephen B. Reid, Project Manager,
Emissions Assessment Group

RE: CCOS Task 3 – Speciation Profile Recommendations – Comparison of Ambient
Measurements to Emissions Representations for Modeling

BACKGROUND

This technical memorandum provides recommendations for updating the speciation profiles used by the California Air Resources Board (ARB) to prepare emission inventories for photochemical air quality modeling efforts. It also describes the data and methods Sonoma Technology, Inc. (STI) used to evaluate these speciation profiles.

Speciation profiles provide a detailed breakdown of the individual chemical species emitted by a specific source category. When an emission inventory is being prepared for use in an air quality model, each source category is assigned a speciation profile to disaggregate total organic gas (TOG) emissions into individual chemical compounds. Incorrect assignments of speciation profiles to emissions sources and/or speciation profiles that do not accurately represent the chemical composition of emissions can cause inaccuracies that will impact photochemical modeling results.

The ARB provided STI with the library of TOG speciation profiles used in the preliminary Central California Ozone Study (CCOS) modeling efforts. Each profile consists of a list of SAROAD¹ codes identifying individual chemical species and the weight fraction of TOG emissions assigned to each species. A short example of a single TOG speciation profile is shown in **Table 1**.

¹ Storage and Retrieval of Aerometric Data (SAROAD).

Table 1. Excerpt from the ARB speciation profile for diesel exhaust emissions.

TOG Profile Number	SAROAD Code	TOG Weight Fraction
818	43203	0.14830287
818	43502	0.14714
818	43201	0.075495
818	43551	0.07507
818	43503	0.07353
818	43206	0.04254
818	98159	0.03799
818	98169	0.0282
818	45202	0.02602753
818	43205	0.02596998
818	43212	0.021833
818	45201	0.02000998
818	43510	0.01867998
818	98078	0.01749
818	43214	0.01623996
818	98132	0.01603418
818	43220	0.01502133
818	43552	0.01476998
818	43202	0.01277507
818	43504	0.0097
...

The ARB also provided a cross-reference file that matches each source category in the CCOS emission inventory with a TOG speciation profile as well as the fraction of reactive organic gas (FROG) for each profile.² An excerpt from this cross reference file is shown in **Table 2**. Background material on the ARB speciation profiles and cross-reference file was obtained from the ARB web site (California Air Resources Board, 2004b). This information was used to evaluate the vintage of each profile and the appropriateness of the profile-to-source category assignments selected by the ARB for application to the year-2000 CCOS inventory.

² The FROG value represents the weight fraction of TOG in a given speciation profile that is considered to be photochemically reactive (California Air Resources Board, 2004a).

Table 2. Excerpt from ARB speciation cross-reference file for mobile source emission categories.

SCC Code	TOG Profile Number	ROG/TOG Fraction	Category Description
1	882	0.8101	Direct Travel Impact Model (DTIM) Default Exhaust
2	877	0.935043	Catalyst Cold Exhaust
3	882	0.8101	Catalyst Hot Exhaust
4	402	0.919587	Non-catalyst Cold Exhaust
5	401	0.9219	Non-catalyst Hot Exhaust
6	422	0.995658	Hot Soak
7	906	0.996504	Diurnal
8	818	0.83671	Diesel Exhaust
9	422	0.995658	Running Evaporatives
10	906	0.996504	Resting Evaporatives
11	906	0.996504	Multi-day Resting Evaporatives
12	906	0.996504	Multi-day Running Evaporatives
15	882	0.8101	Catalyst Bus
16	401	0.9219	Non-catalyst Bus
17	818	0.83671	Diesel Bus
18	882	0.8101	Catalyst Idle
19	401	0.9219	Non-catalyst idle
20	818	0.83671	Diesel Idle

TECHNICAL APPROACH

The ARB speciation profile library contains 425 organic gas profiles, making a detailed analysis of each profile impractical. Therefore, an effort was made to prioritize the profiles by the magnitude of emissions assigned to each profile and relative ozone reactivity so that analyses could be focused on the most important profiles. The emissions associated with each profile were determined using a gridded, weekday emission inventory³ for July 31, 2000, provided by the ARB. For assessing speciation profiles, the ARB provided STI with the anthropogenic emission inventory developed for the CCOS study domain. In that inventory, TOG emissions were disaggregated using 252 speciation profiles. To determine priorities for further evaluation, we converted TOG emissions to reactive organic gas (ROG) emissions by using the FROG values listed in the ARB speciation cross-reference file. We then summed the ROG emissions across source categories assigned to each profile to obtain total ROG emissions by speciation profile.

³ This was the placeholder emission inventory used for preliminary modeling efforts for the July 29–August 2, 2000, episode. The ARB applied “gross adjustments” to this inventory to approximate planned inventory improvements, including updates to the EMFAC and OFFROAD models used to estimate emissions from on-road and off-road mobile sources.

The reactivity of each profile was estimated using published maximum incremental reactivity (MIR) values that are used to represent the ozone formation potential of various organic compounds (Carter, 2003). Weighted reactivity values for each profile were calculated as follows:

$$R = \sum_{i=1}^n (\text{MIR})_i w_i$$

where:

- R = weighted reactivity
- (MIR)_i = maximum incremental reactivity for species *i*
- w_i = weight fraction of species *i* in a given profile

The resulting reactivity values for each speciation profile were multiplied by the total of TOG emissions associated with each profile to produce total reactivity-weighted emissions by profile. **Table 3** shows the total TOG-, ROG-, and MIR-weighted emissions by speciation profile for those profiles with the highest contribution to total MIR-weighted emissions. As shown in Table 3, the top 10 profiles—which are mostly associated with mobile source exhaust and evaporative emissions—account for 80% of the MIR-weighted TOG emissions in the CCOS domain (as well as 52% of the total TOG emissions and 66% of the total ROG emissions⁴). These results suggest that focusing on as few as 10 (or 4%) of the 252 speciation profiles used in the CCOS inventory would address the speciation of 80% of the MIR-weighted TOG emissions. Adding the next four profiles account for an additional 5% of the MIR-weighted emissions. The remaining 238 speciation profiles account for the last 15% of emissions.

Speciation profiles associated with natural sources, such as wildfires and biogenic emissions, can have substantial air quality effects and, thus, are normally included in emission inventories used as model inputs. The gridded emission inventory provided by the ARB for our use in this study contained day-specific wildfire emissions for July 31, 2000, a date when a large wildfire was burning in the southern San Joaquin Valley. The actual TOG emissions from wildfires for this day were 1,988 tons per day, about 50% of the total TOG emissions from all anthropogenic sources.

⁴ ROG and TOG emissions were also evaluated without any reference to speciation profiles or reactivity weighting. The only top 10 ROG source not addressed in the MIR-weighted rankings is pesticide application, a source category for which ARB has recently developed a new profile. Key TOG sources that contribute relatively insignificant amounts to the MIR-weighted TOG emissions include landfills and natural gas distribution.

Table 3. Anthropogenic TOG-, ROG-, and MIR-weighted TOG emissions by speciation profile.

Rank	Profile Number	Profile Name	TOG (tons/day)	ROG (tons/day)	Weighted Reactivity	MIR-Weighted TOG	MIR-Weighted TOG %	Cumulative MIR-Weighted TOG %
1	401	Gasoline – non-catalyst – stabilized exhaust	241	222	4.4	1,053	21%	21%
2	882	Gasoline – catalyst – stabilized exhaust	179	145	3.4	618	12%	34%
3	422	Hot soak emissions – California light-duty vehicles	198	197	2.4	475	10%	43%
4	818	Farm equipment – diesel – light- and heavy-duty vehicles	95	79	5.0	470	10%	53%
5	877	Gasoline – catalyst – FTP bag 1-3 (starts)	102	96	3.9	401	8%	61%
6	203	Animal waste decomposition	1,095	88	0.3	322	7%	67%
7	586	Composite jet exhaust JP-5	25	22	7.0	172	3%	71%
8	906	Gasoline – diurnal & resting evaporatives	87	86	2.0	172	3%	74%
9	419	Liquid gasoline – MTBE 11% – commercial grade	57	57	2.7	152	3%	78%
10	402	Gasoline – non-cat – FTP bag 1-3 (starts)	31	28	3.8	116	2%	80%
11	783	Industrial surface coating – solvent based paint	28	28	2.8	79	2%	81%
12	600	Species unknown – all category composite	42	29	1.5	61	1%	83%
13	716	Medium cure asphalt	22	22	2.4	53	1%	84%
14	1902	Architectural coatings – water borne	24	24	2.0	48	1%	85%
—	All Other	Various	1,794	418	0.4	754	15%	100%
		Total	4,017	1,540	—	4,946	100%	—

The files received from the ARB did not include a day-specific biogenic emission inventory; therefore, for comparison purposes, we used the ARB's California Emissions Forecasting System (CEFS) web site to estimate biogenic TOG emissions for the CCOS domain at 2,800 tons per day (about 70% of the total TOG emissions from all anthropogenic sources). Biogenic emissions of isoprene, monoterpenes, and methyl butanol are calculated directly within the ARB's BEIGIS model, making speciation profiles unnecessary. However, before biogenic emissions are input to air quality models, the total emissions are increased by 30% to account for "other volatile organic compounds" (OVOCs). These additional emissions are currently speciated using a profile developed from measurements taken above a Sierra Nevada Ponderosa Pine Plantation, although the ARB may use BEIS-3 to estimate emissions from these additional compounds in the future (California Air Resources Board, 2005b).

The following sections contain specific information about the "top" 10 MIR-weighted emissions speciation profiles plus the ARB wildfire profile, along with suggestions for alternative profiles we have identified. We also comment on the remaining individual profiles of merit making up the cumulative total of 85% of the MIR-weighted emissions.

RANK 1: PROFILE 401 (GASOLINE – NON-CATALYST – STABILIZED EXHAUST)
RANK 2: PROFILE 882 (GASOLINE – CATALYST – STABILIZED EXHAUST)

Background

Profiles 401 and 882 are used to speciate exhaust emissions from on-road gasoline vehicles (non-catalyst and catalyst, respectively). In addition, profile 401 is applied to various types of gasoline-powered off-road equipment, such as recreational boats and lawn and garden equipment (see **Figure 1**). These profiles were derived from tests conducted during 1994 and 1996 through the ARB's in-use vehicle surveillance program. The objective of this ongoing test program is to determine a fleet "snapshot" of baseline mobile source emissions, including the development of exhaust and evaporative speciation profiles for in-use vehicles (California Air Resources Board, 2005a).

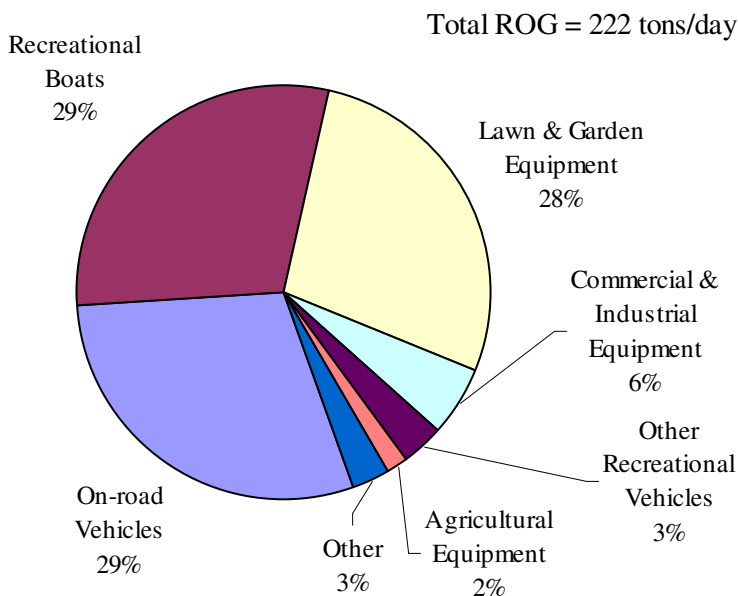


Figure 1. ROG emissions associated with ARB profile 401 by source type.

Analysis

Recent studies have shown that the introduction of reformulated gasoline (RFG) in California has affected the reactivity of exhaust organic gas emissions from motor vehicles. Measurements taken at the Caldecott tunnel⁵ in the San Francisco Bay Area as part of a University of California (UC), Berkeley study show a 6% reduction in the reactivity⁶ of tunnel non-methane organic compound (NMOC) emissions between 1995 and 1996, the year when Phase 2 RFG requirements first took effect (Harley and Kean, 2004).

The ARB speciation profiles for exhaust emissions from gasoline-fueled vehicles appear to reflect these changes to California fuels. **Figure 2** shows weighted reactivity values for ARB profiles for stabilized emissions from non-catalyst (401) and catalyst (882) vehicles and for profiles derived from tunnel measurements in 1999 and 2001. The reactivity values derived from tunnel measurements fall between the values for these two ARB profiles, which is to be expected because tunnel measurements reflect a mixture of gasoline vehicle types. **Figure 3** shows the composition of these profiles by species group, and one can see that there is good general agreement between the ARB profiles and the profiles developed from tunnel measurements. Differences between the profiles, such as the higher fraction of isoalkanes in the tunnel profiles, can likely be explained by the presence of running loss evaporative emissions as well as exhaust emissions in the tunnel measurements.

⁵ Caldecott tunnel measurements were taken in bore two of the tunnel, where heavy trucks are not allowed.

⁶ Reactivity assessments were made using the maximum incremental reactivity scale described above.

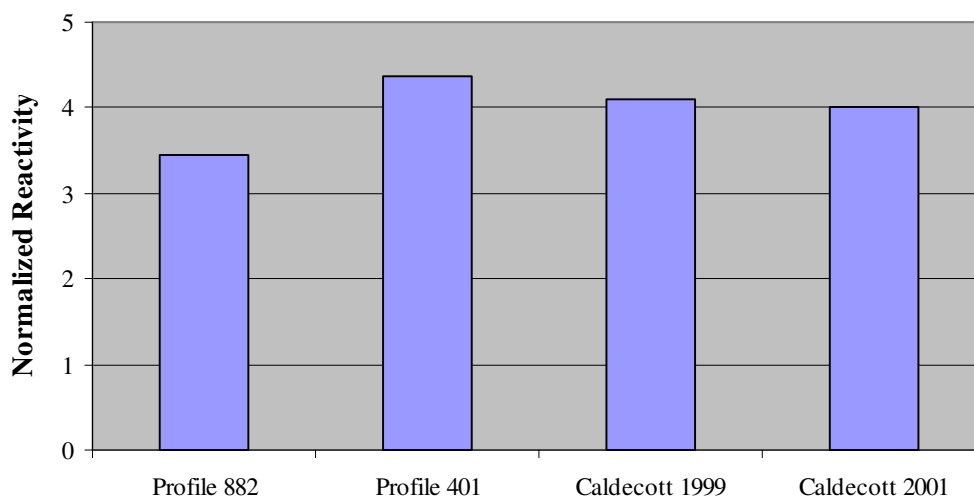


Figure 2. Weighted reactivity of various profiles for gasoline-fueled vehicles.

Note that profile 401 is also applied to off-road mobile sources, with over 70% of the organic gas emissions associated with this profile being attributable to off-road sources, such as recreational boats and lawn and garden equipment (see Figure 1). To investigate possible differences in the composition of organic gas emissions from on-road and off-road mobile sources, a literature search was undertaken to identify exhaust speciation profiles for off-road sources. A 1997 study characterized emissions from 10 four-stroke lawn mower engines and developed exhaust speciation profiles based on tests conducted with a 1990 national average blend gasoline and a California Phase 2 reformulated gasoline (Gabele, 1997). The profile based on the California fuel is similar to ARB profile 401, although it contains significantly higher fractions of methane and acetylene (see Appendix). Overall, the weighted reactivity of the Gabele profile is 4.2—slightly lower than the weighted reactivity value of 4.4 for profile 401.

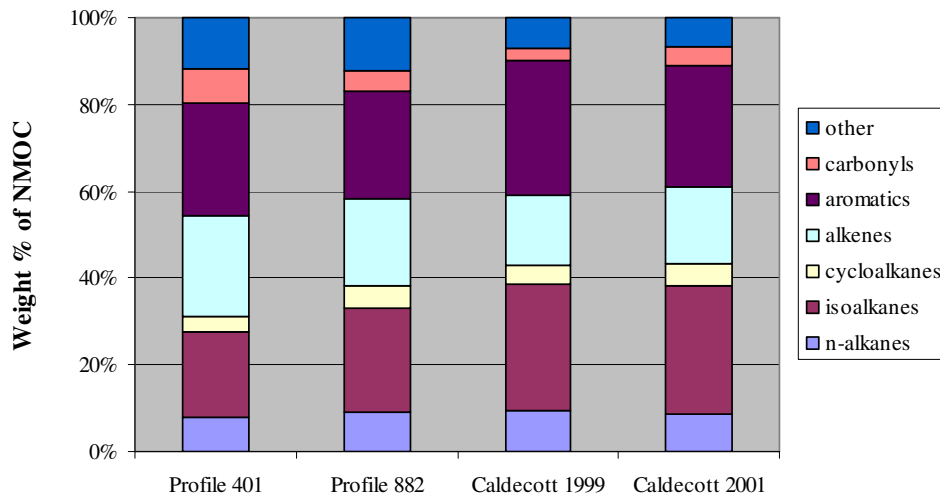


Figure 3. Composition of emissions from gasoline-fueled vehicles by species group.

Recommendations

ARB profiles 401 and 882 appear to be appropriate for year-2000 exhaust emissions from gasoline-fueled on-road mobile sources in California. However, the speciation profile developed by Gabele was derived from source tests conducted on off-road equipment (lawn mowers) using California reformulated gasoline and is preferable for gasoline-powered off-road mobile sources. Use of this profile would lower the reactivity of speciated emissions from these sources by approximately 5%.

RANK 3: PROFILE 422 (HOT SOAK EMISSIONS – CALIFORNIA LIGHT-DUTY VEHICLES)

Background

Profile 422 is used to speciate running and hot soak⁷ evaporative emissions from light-duty gasoline vehicles. The profile is based on 19 hot soak Sealed Housing for Evaporative Determination (SHED) tests conducted in 1999 and 2000 (Hsu, 2003).

Analysis

The ARB has recently updated the speciation profile for hot soak emissions. Profile 422 replaces profile 420, which was based on 1997 SHED tests, and the new profile contains significantly lower fractions of toluene, xylenes, and benzene than profile 420. The overall reactivity of profile 422 is 2.2, as compared to a reactivity of 3.1 for profile 420.

Recommendation

Profile 422 is a recent profile based on source tests conducted in 1999 and 2000 and, as such, is an appropriate choice for running and hot soak evaporative emissions from light-duty gasoline vehicles in California in 2000.

RANK 4: PROFILE 818 (DIESEL FARM EQUIPMENT)

Background

In the CCOS emission inventory, profile 818 is applied to exhaust emissions from both on-road and off-road diesel vehicles (see **Figure 4**). The profile is based on a 1991 study conducted at California Polytechnic State University, San Luis Obispo in which engine exhaust emissions were collected from heavy-duty diesel equipment, such as tractors (Censullo, 1991).

Analysis

The chemical composition of emissions from on-road and off-road diesel engines may vary because of differing regulatory requirements, operating modes, and maintenance schedules

⁷ Hot soak emissions are evaporatives emitted during the time an engine is cooling down following vehicle shut-off.

(Fitz et al., 2004), so the applicability of profile 818 to on-road diesel vehicles is questionable. Therefore, a number of organic gas speciation profiles for on-road diesel vehicles were identified through a literature search and compared to ARB profile 818. U.S. Environmental Protection Agency (EPA) profile 2520 was derived from measurements of vehicle exhaust taken at the Tuscarora Tunnel in Pennsylvania in 1995 (U.S. Environmental Protection Agency, 2002). During a recent receptor modeling study conducted for CCOS, the Desert Research Institute (DRI) used a diesel exhaust profile derived from 1996 tunnel measurements in Baltimore and New York (Fujita et al., 2005). A recent Lake Michigan Air Directors Consortium (LADCO) study cites an organic gas profile for on-road diesel engines developed by Schauer in 1999 (Schauer et al., 1999) through the use of dynamometer testing of two medium-duty diesel trucks from the 1996 in-use vehicle fleet in Southern California. These trucks were fueled with California reformulated diesel fuel.. **Figure 5** shows the weighted reactivity for each of these profiles, along with ARB profile 818. The reactivity of the ARB profile is 12% lower than the EPA and DRI profiles and 12% higher than the Schauer profile. However, the Schauer profile contained a significant fraction of unidentified species; therefore, this reactivity value may not be accurate. All evaluated diesel profiles can be seen in the Appendix.

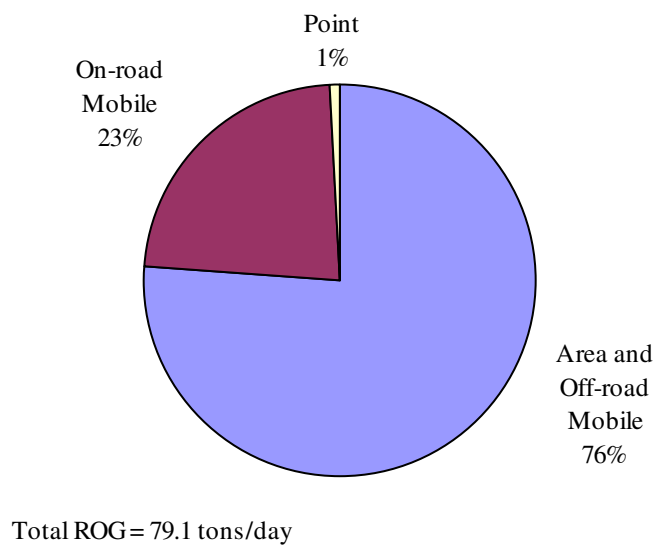


Figure 4. ROG emissions associated with ARB profile 818 by source type.

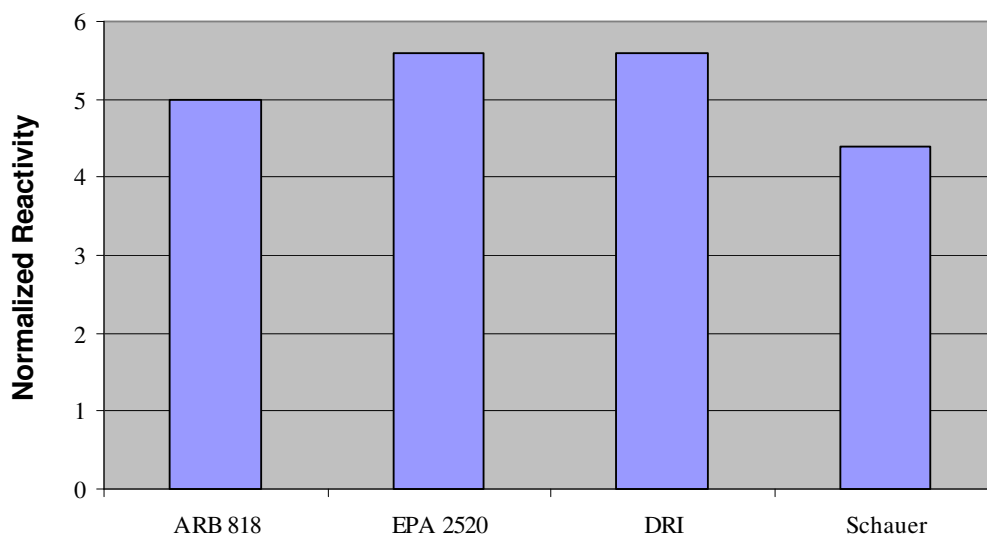


Figure 5. Weighted reactivity of various diesel exhaust profiles.

Recommendations

It is recommended that separate speciation profiles be used for on-road and off-road mobile sources because speciation profiles developed specifically for on-road diesel engines appear to have a higher weighted reactivity than the ARB diesel profile. The Schauer profile was developed through tests on trucks from California's vehicle fleet using California reformulated diesel fuel, so it is recommended that this profile be used to speciate on-road diesel emissions for future CCOS modeling efforts. However, the Schauer profile contains a significant fraction of unidentified compounds (18%), and it may be necessary to disaggregate this unidentified fraction to likely known compounds. The Appendix lists each of the diesel profiles discussed in this section.

RANK 5: PROFILE 877 (GASOLINE – CATALYST – FTP BAG 1-3 STARTS)

RANK 10: PROFILE 402 (GASOLINE – NON-CATALYST – FTP BAG 1-3 STARTS)

Background

ARB profiles 877 and 402 are applied to cold-start emissions from gasoline-fueled on-road vehicles. These profiles were derived from tests conducted during 1994 and 1996 through the ARB's in-use vehicle surveillance program. This objective of this ongoing test program is to determine a fleet "snapshot" of baseline mobile source emissions, including the development of exhaust and evaporative speciation profiles for in-use vehicles (California Air Resources Board, 2005a).

Analysis

Recent studies have shown that the introduction of RFG in California has affected the reactivity of exhaust organic gas emissions from motor vehicles. Laboratory dynamometer tests conducted with various gasoline blends have shown that, on average, the exhaust reactivity for California Phase 2 fuels was the lowest among seven fuels tested for cold start emissions and was 16% lower than the highest fuel type (Ho and Winer, 1998).

Figure 6 shows weighted reactivity values of ARB profiles for start emissions and for profiles derived from tests performed on 19 in-use passenger cars and light-duty trucks during the Ho and Winer study. The ARB profiles for start emissions from non-catalyst (402) and catalyst (877) vehicles were derived by subtracting bag 3 emissions from bag 1 emissions so that the speciation profiles reflect excess emissions during the first 100 seconds of cold start. The reactivity values for the ARB profiles are very close to the reactivity value for bag 1 emissions derived from Ho and Winer.

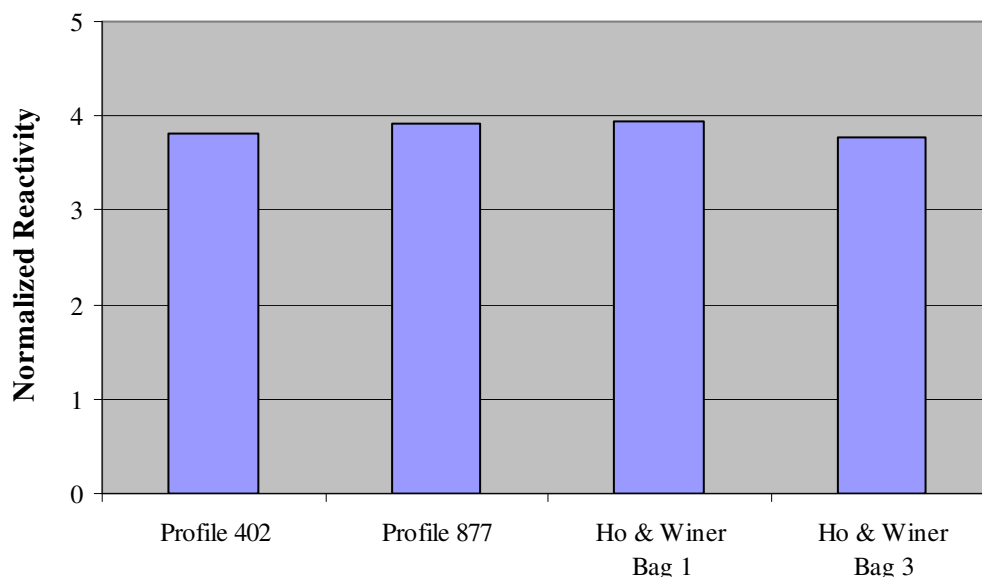


Figure 6. Weighted reactivity of various profiles of start emissions from gasoline-fueled vehicles.

Recommendations

These results support the appropriateness of the ARB profiles applied to cold start emissions from gasoline vehicles in the CCOS inventory. It is recommended that these profiles be used for future year-2000 CCOS modeling efforts.

RANK 6: PROFILE 203 (ANIMAL WASTE DECOMPOSITION)Background

ARB profile 203 is applied to organic gas emissions from livestock husbandry operations in the CCOS domain. Almost half these emissions are associated with dairies and another 25% are associated with range cattle. Profile 203 is taken from the EPA's SPECIATE 3.2 database and is based on a 1978 study in the South Coast Air Basin (U.S. Environmental Protection Agency, 2002).

Analysis

Over 1,000 tons per day of TOG emissions are associated with profile 203, but only 88 tons per day of ROG (see Table 3). This means that the FROG assumed for this profile is extremely important, as a change of only 1% in the FROG value would result in a change of over 10 tons per day in the ROG emissions from animal waste decomposition. Profile 203 is shown in **Table 4**, and the species methane, ethane, and acetone are judged to be non-reactive by the ARB, resulting in a FROG value of 8% for this profile.

Table 4. ARB TOG profile for animal waste decomposition.

Species Name	CAS Code	Weight Percent	MIR
Methane	74-82-8	70	0.0139
Ethane	74-84-0	20	0.31
Acetone	67-64-1	2	0.43
Isopropyl alcohol	67-63-0	2	0.71
Propyl acetate	109-60-4	2	0.86
Ethanol	64-17-5	2	1.69
Trimethyl amine	75-50-3	1	7.06
Ethyl amine	75-04-7	1	7.79

The CCOS group recently sponsored a field study at a northern California dairy to evaluate emissions of TOG and ROG (Schmidt et al., 2005). Measurements were taken for a variety of processes on a summer day when 3,442 cows were present at the facility. **Table 5** shows TOG and ROG emission rates by process and the fraction of reactive organic gas value for each process. The FROG value varied widely among the processes, and overall, the ratio of ROG-to-TOG was 0.8%, or one-tenth of the fraction assumed for profile 203.

Table 5. Dairy organic gas emissions by process (based on a population of 3,442 cows).

Process Type	Process	Emissions (lbs/day)		ROG Percent
		TOG	ROG	
Milk Cow	Bedding	1.3	0.5	38.5%
	Flush Lane	10.5	1.4	13.3%
	Feeding	5.7	5.4	94.7%
	Turnout	500.5	2.1	0.4%
Dry Cow	Bedding	0.0	0.0	0.0%
	Flush Lane	0.1	0.1	100.0%
	Feeding	0.5	0.4	80.0%
	Turnout	0.7	0.7	100.0%
Solids Piles	Fresh	3.1	0.0	0.0%
	Aged	873.4	0.0	0.0%
	Bedding Storage	0.5	0.3	60.0%
Lagoon	Lagoon	164.1	1.1	0.7%
Milk Parlor	Effluent Stream	0.2	0.2	100.0%
Total	All Processes	1560.6	12.2	0.8%

Recommendations

Significant uncertainty exists in the composition of emissions from animal waste decomposition, and further study of this source category is needed. California State University at Fresno is currently under contract with the ARB to evaluate reactive organic gas emissions at California dairies. This project involves the chemical speciation of TOG samples collected at dairies, and project completion is expected in December 2005 (California Air Resources Board, 2005c). It is recommended that the results of this study be evaluated for inclusion to the ARB speciation database, and that ARB profile 203 continue to be applied to animal waste decomposition emissions in the meantime.

RANK 7: PROFILE 586 (COMPOSITE JET EXHAUST)

Background

ARB profile 586 is applied to emissions from military, commercial, and civil jet aircraft in the CCOS inventory. Profile 586 is a composite of three EPA profiles (1097-1099) that were developed from engine tests conducted in 1984 on a CFM-36 jet engine fired with JP-5 fuel at various power settings. Data collected were combined according to average landing-and-takeoff (LTO) cycle times published in AP-42. JP-5 fuel is primarily used in military aircraft, whereas commercial aircraft use Jet A (United States) or Jet A-1 fuel (outside the United States), although all three fuels are kerosene-type fuels differing mostly in their flashpoints and freezing points (Chevron, 2005).

Analysis

Environment Canada (EC) has compiled a composite emissions profile for jet aircraft engines based on engine exhaust stream measurements taken at Macdonald-Cartier International Airport in Ottawa, Canada, during 1993 and 1994 (Cantox Environmental Inc., 2004). These tests were conducted at various engine speeds on aircraft using Jet A-1 fuel. **Figure 7** shows a comparison of ARB profile 586 and the EC profile by species group. About 20% of both profiles is comprised of the carbonyl compounds formaldehyde and acetaldehyde, but carbonyl acetone makes up 64% of the EC profile—making carbonyls the dominant species group. The ARB profile contains larger fractions of alkenes (especially ethylene) and alkanes (especially methane) than the EC profile. Also, the weighted reactivity of the EC profile is only 3, compared to 7 for the ARB profile—largely because of the low reactivity of acetone. These differences may reflect changes in the composition of jet fuels produced since the mid-1990s (Cantox Environmental Inc., 2004).

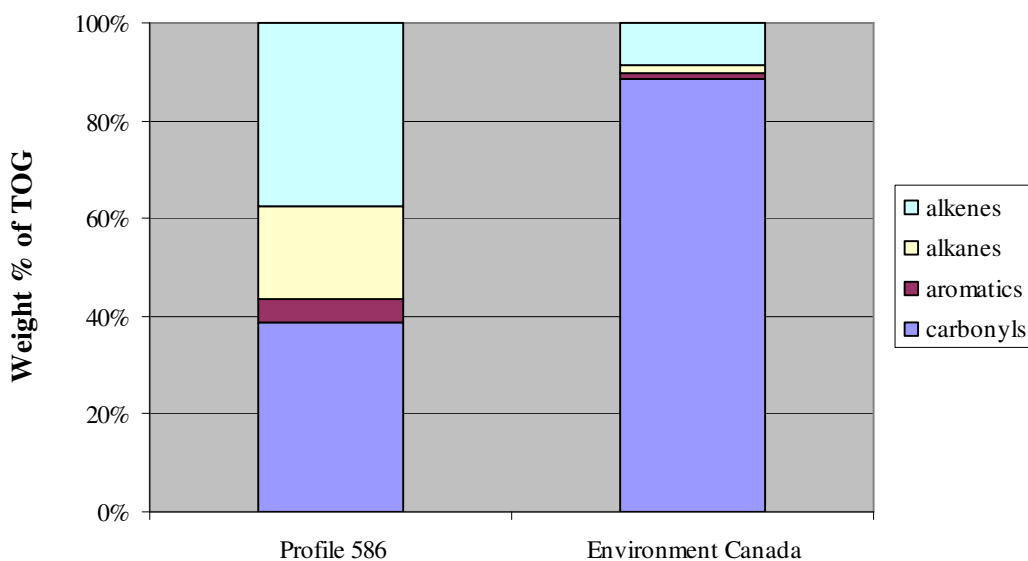


Figure 7. Composition of organic gas emissions from jet aircraft engines by species group.

Recommendations

The ARB profile used for jet engine exhaust dates to 1984 and is based on source tests conducted using a fuel that is not in use among commercial aircraft. The more recent Canadian study suggests that fuel composition changes may have significantly altered the makeup of emissions from jet engines since the mid-1980s, although this study was performed at an airport rather than under laboratory conditions. Further research is needed to determine the composition of TOG emissions from jet engines using fuels common to California in 2000. It is recommended that ARB profile 586 continue to be applied to jet exhaust emissions until better data is available.

RANK 8: PROFILE 906 (GASOLINE – DIURNAL AND RESTING EVAPORATIVES)
RANK 9: PROFILE 419 (LIQUID GASOLINE – MTBE 11% – COMMERCIAL GRADE)

Background

ARB profile 906 is applied to diurnal and resting evaporative emissions from gasoline-fueled on-road mobile sources in the CCOS inventory, as well as a variety of gasoline storage-related categories. Profile 906 is based on a headspace vapor⁸ composition estimated from the composition of liquid gasoline using vapor-liquid equilibrium theory. This study was performed using gasoline samples collected at service stations in Berkeley, California, during the summer of 1996 (Harley and Kean, 2004).

ARB profile 419 is assigned to spillage losses from vehicle refueling and petroleum marketing operations in the CCOS inventory. This profile is based on a 1997 ARB study of gasoline blends containing methyl tert-butyl ether (MTBE) and ethanol and assumes an MTBE content of 11% by volume.

Analysis

The UC Berkeley study cited earlier (Harley and Kean, 2004) derived speciation profiles from samples of liquid gasoline collected at service stations in Berkeley, California, during the summers of 1995, 1996, 1999, and 2001 and in Sacramento, California, during the summer of 2001. This study showed that large changes in fuel composition took place between 1995 and 1996 because of California Phase 2 RFG requirements (Harley and Kean, 2004). Also, gasoline in the San Francisco Bay Area shows a decline in the use of oxygenates (particularly MTBE) after 1996, while the oxygenate content in Sacramento, California, remains at 1996 levels. Federal RFG program requirements mandate the use of oxygenates in the Central Valley but not the San Francisco Bay Area, which may explain these differences in oxygenate use. However, the weighted reactivity of gasoline samples from Berkeley and Sacramento show little difference, although both are about 20% higher than the reactivity of ARB profile 419 (see **Figure 8**).

Similarly, the UC Berkeley study shows that the reactivity of emissions from gasoline headspace vapors decreased sharply between 1995 and 1996 but has remained almost constant since 1996 (see **Figure 9**). ARB profile 906 is based on the 1996 UC Berkeley headspace profile.

⁸ “Headspace” refers to the portion of a vehicle’s fuel tank that is unused. Vapors trapped in this portion of the tank are displaced when the tank is filled.

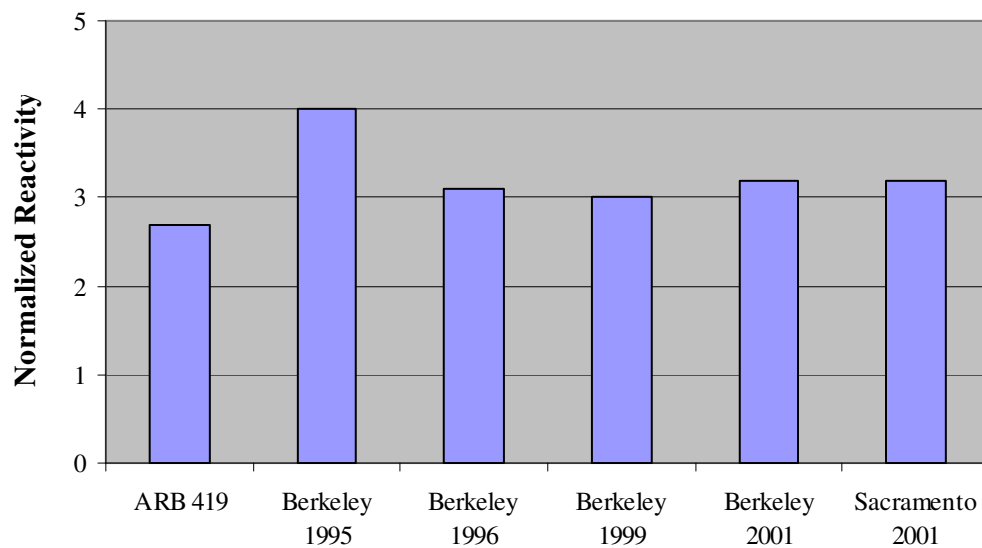


Figure 8. Weighted reactivity of liquid gasoline speciation profiles.

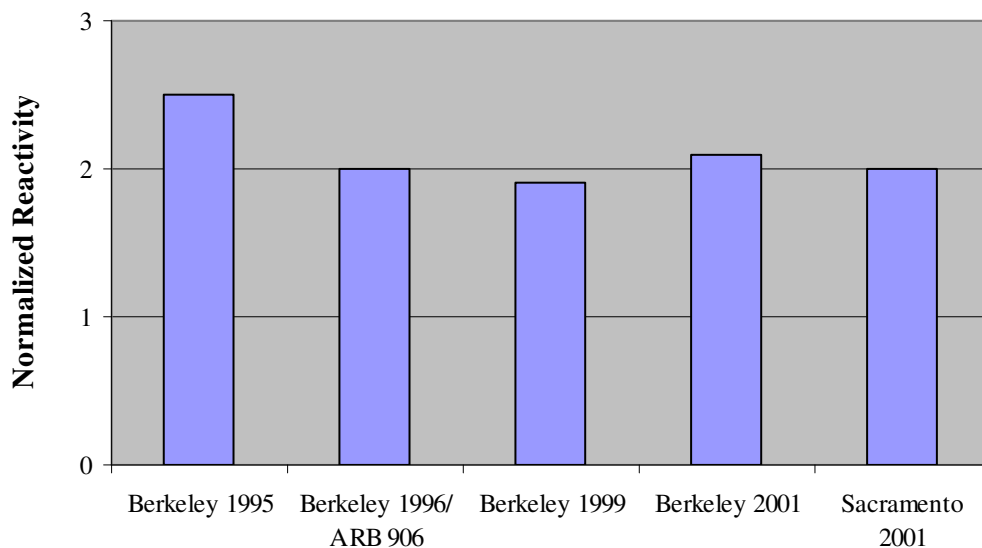


Figure 9. Weighted reactivity of gasoline headspace speciation profiles.

Recommendations

Speciation profiles for evaporative emissions from gasoline-fueled vehicles and gasoline storage and transfer operations appear to be appropriate for conditions in California in 2000. It is recommended that profiles 906 and 419 be used for future year-2000 CCOS modeling efforts.

UNRANKED: PROFILE 307 (FOREST FIRES)Background

ARB profile 307 is applied to unplanned wildfires on grasslands and woodlands in the CCOS domain. This profile is taken from the EPA's speciated 3.2 database and is based on a literature search conducted in 1975 (U.S. Environmental Protection Agency, 2002). This profile is also the default speciation profile for forest wildfires used in the EPA's SMOKE emissions modeling system.

Analysis

A literature search did not uncover any California-specific data on the composition of emissions from wildfires. However, a 2002 paper on the speciation of gas-phase emissions from the burning of foliar fuels (Hays et al., 2002) provides speciation profiles for five biomass types, including western hemlock and ponderosa pine, and LADCO recently developed wildfire speciation profiles based on data compiled at the National Fire Emissions Technical Workshop held in May 2004 (Battye and Harris, 2005). LADCO developed a profile for forest wildfires and another for grassland wildfires, and both profiles differ widely from ARB profile 307. For example, the LADCO profiles contain significant fractions of aldehydes, such as formaldehyde and acetaldehyde, none of which appear in the ARB profile. Also, the weighted reactivity of the LADCO profiles is 11-16% lower than the weighted reactivity of the ARB profile (see **Figure 10**).

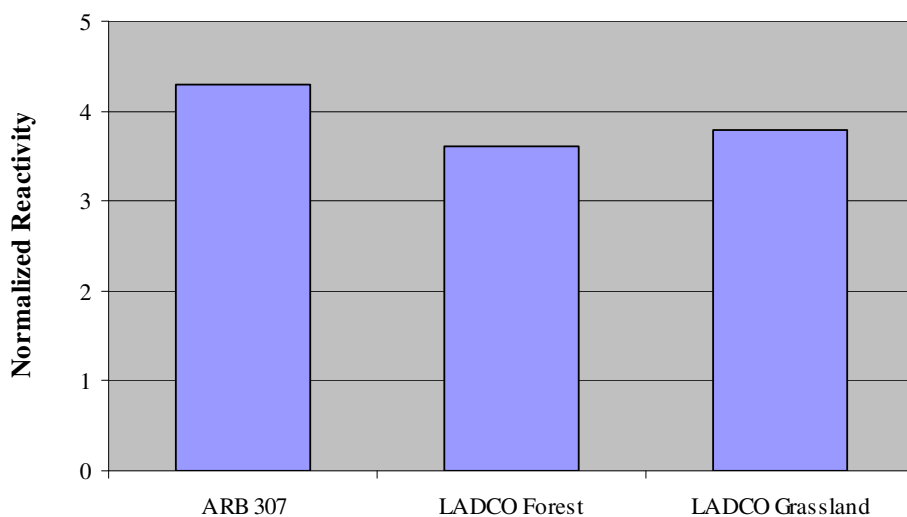


Figure 10. Weighted reactivity for wildfire speciation profiles.

Recommendations

Wildfires can be a significant source of ROG emissions on certain days, and the speciation profile for this source category dates to 1975. Therefore, it is recommended that a

new profile be developed that reflects vegetation types commonly burned during wildfires in California. The 2002 paper cited above and the data used by LADCO to develop speciation profiles for fires on forested lands and grasslands are sources of data that could be used for this profile development. The profiles developed by LADCO are listed in the Appendix alongside ARB profile 307.

OTHER PROFILES

In addition to the high-priority speciation profiles discussed above, STI performed a brief analysis on four additional profiles that were associated with at least 1% of the MIR-weighted TOG emissions in the CCOS domain, as well as the profile used to speciate biogenic emissions of OVOC.

Profiles 783 and 906 – Surface Coatings

ARB profile 906 (water-borne architectural coatings) is based on a 1998 architectural coatings survey conducted by ARB. During this study, questionnaires were sent to over 700 companies that potentially sold architectural coatings in California in 1996, and data were collected on sales and coating composition (California Air Resources Board, 1999). ARB conducts this survey every four to five years, and a 2001 survey gathered data on architectural coatings sold in California during 2000.

ARB profile 783 (industrial surface coatings) was developed during a 1985 emission inventory improvement project in the South Coast Air Basin (Oliver and Peoples, 1985). As part of this study, samples of the most widely used coating types were obtained from surface coating facilities and analyzed. This profile is applied to a variety of source categories in the CCOS inventory, including metal can, coil, and wood furniture coating.

LADCO has recently developed profiles for several surface coating categories, including wood furniture coating, can coating, and miscellaneous manufacturing. LADCO updated surface coating profiles from EPA's speciated 3.2 database using the current usage of various solvents such as toluene and xylene across the entire coating formulation industry, as reported by the Freedonia Group (Battye and Harris, 2005). These adjustments were designed to reflect recent changes in solvent composition due to market changes or regulatory requirements. **Figure 11** shows the weighted reactivity of these updated profiles is about 30% lower than the weighted reactivity for ARB profile 783. It is recommended that these LADCO profiles be used for future CCOS modeling efforts, although some adjustments to the national-level data used to create these profiles may be necessary to reflect conditions in California. The recommended LADCO profiles are listed in the Appendix alongside ARB profile 783.

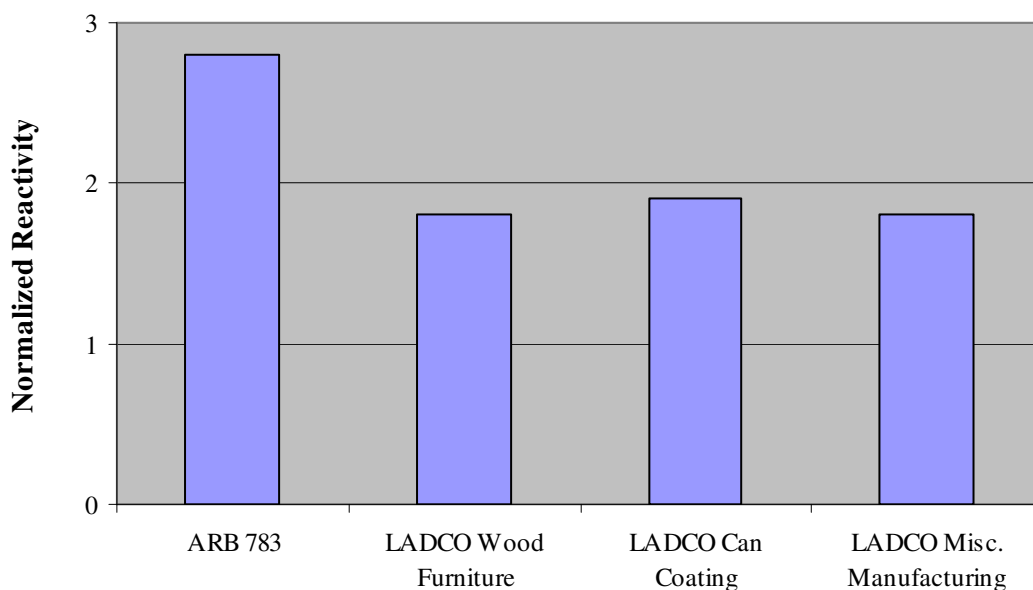


Figure 11. Weighted reactivity for emissions from industrial surface coatings.

Profile 716 – Medium Cure Asphalt

ARB profile 716 (medium cure asphalt) was also developed during the 1985 emission inventory improvement project (Oliver and Peoples, 1985). The profile was developed from analysis of composite asphalt samples, but it was later determined that some of the samples were purposely altered at a refinery before shipment. This study is also the basis for the asphaltic concrete profile in the EPA's SPECIATE 3.2 database (profile #1007). A literature search did not locate a more recent speciation profile for this source category.

Profile 600 – All Category Composite

ARB profile 600 represents a weighted composite across all profile categories. This profile is applied to over 90 organic gas emission source categories in the CCOS emissions inventory. **Figure 12** shows a breakdown by source category of ROG emissions associated with profile 600; a wide variety of source types are included, ranging from evaporative sources to fuel combustion.

The relative importance of profile 600 may indicate that it is being applied too broadly in the CCOS inventory. An alternative approach would be to develop multiple composite profiles: one for fuel combustion categories, one for solvent usage, and one for miscellaneous processes.

Biogenic OVOC Profile

Biogenic emissions of isoprene, monoterpenes, and methyl butanol are calculated directly within the ARB's BEIGIS model, making speciation profiles unnecessary. However, before biogenic emissions are input to air quality models, the total emissions are increased by 30% to

account for OVOCs. These additional emissions are currently speciated using a profile developed from measurements taken above a Sierra Nevada Ponderosa Pine Plantation, and a literature review did not result in the identification of an improved profile for this source type.

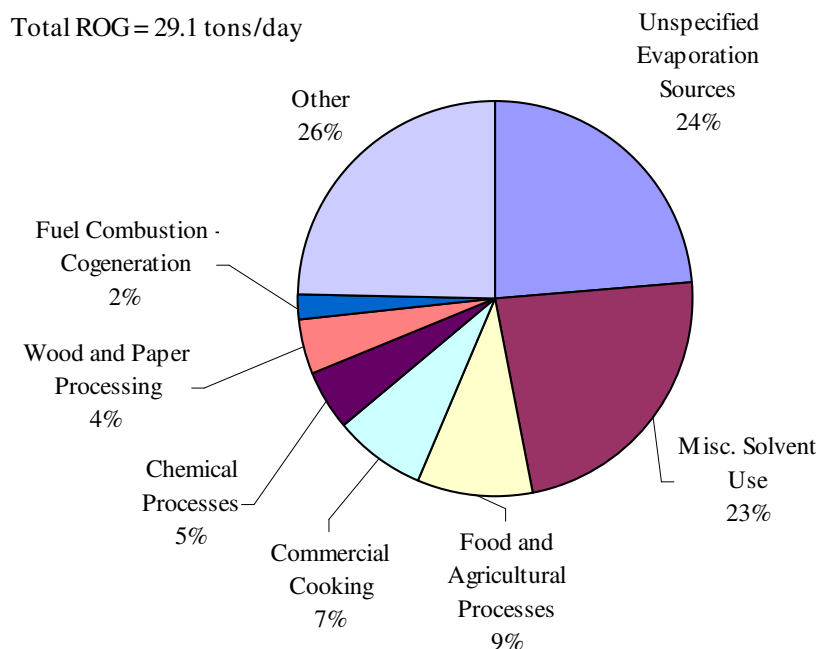


Figure 12. ROG emissions associated with ARB profile 600 by source type.

SUMMARY OF FINDINGS AND RECOMMENDATIONS

A major finding of these analyses is that, while the ARB organic gas profile database contains hundreds of speciation profiles, only a handful of them appear to be significantly affecting the preparation of the CCOS emission inventory for modeling. Ten profiles (or 4% of the total number of profiles applied to the CCOS inventory) account for 80% of the MIR-weighted TOG emissions in the CCOS inventory. This greatly narrows the focus for pending speciation profile research and improvements. Specific findings and recommendations related to these 10 high-priority (and other) profiles include

- Speciation profiles applied to exhaust and evaporative emissions from gasoline-fueled vehicles appear to be appropriate for conditions in California in 2000. However, the speciation profile for non-catalyst vehicles (profile 401) is also applied to off-road mobile sources such as recreational boats and lawn and garden equipment. It is recommended that an exhaust profile from a 1997 study that characterized emissions from 10 four-stroke lawn mower engines fueled with a California Phase 2 RFG be applied to gasoline-fueled off-road mobile sources.
- The current ARB profile for exhaust emissions from diesel engines was based on testing of off-road farming equipment. Separate speciation profiles should be used for on-road and off-road mobile sources, as speciation profiles developed specifically for on-road

diesel engines appear to have a higher weighted reactivity than the ARB diesel profile. It is recommended that the Schauer diesel profile listed in the Appendix be used for future CCOS modeling efforts.

- Uncertainty exists in the composition of emissions from animal waste decomposition, and further study of this source category is needed. A recent study by Schmidt shows the reactive fraction of TOG emissions from a northern California dairy varying by process type, and the overall reactive fraction of TOG emissions in the Schmidt study is only 10% of the reactive fraction of the ARB TOG profile currently assigned to this source category.
- The ARB profile used for jet engine exhaust dates to 1984 and is based on source tests conducted using a fuel not in use among commercial aircraft. A more recent Canadian study suggests that fuel composition changes may have significantly altered the makeup of emissions from jet engines since the mid-1980s, although this study was performed at an airport rather than under laboratory conditions. More study is needed to determine the composition of TOG emissions from jet engines using current fuels.
- Wildfires can be a significant source of ROG emissions on specific days, and the speciation profile for this source category dates to 1975. It is recommended that a new profile be developed, similar to the process recently undertaken by LADCO, based on vegetation types common to California.
- The ARB profile used for industrial surface coatings is based on a 1985 study, and recent work by LADCO suggests that the composition of such coatings has changed significantly since the mid-1980s, resulting in a lowering of the reactivity of emissions from industrial surface coatings by as much as 30%. It is recommended that the LADCO profiles be used for future CCOS modeling efforts, although some adjustment to these profiles may be required to reflect conditions in California.
- The ARB profile used for medium-cure asphalt is based on a 1985 study that relied on the analysis of asphalt samples later determined to have been purposely altered at a refinery before shipment. A new speciation profile for this source category should be developed from current asphalt samples.
- ARB's all category composite speciation profile is applied to a wide variety of source categories in the CCOS inventory. Table 3 shows that the weighted reactivity of speciation profiles for fuel combustion processes tends to be higher than the reactivity of profiles for evaporative sources. Therefore, it is recommended that multiple composite profiles be developed according to broad source types such as fuel combustion and solvent usage.

The recommended profiles cited above can be found in the Appendix of this memorandum. As an initial step toward implementing these recommendations and evaluating their impact, air quality model sensitivity runs could be performed using an emission inventory that has been speciated with the updated profiles. To assess the potential impact of such changes, the anthropogenic emission inventory shown in Table 3 has been re-weighted using MIR values from recommended profiles that could be immediately incorporated into the CCOS modeling efforts. Also, exhaust emissions associated with profiles 401 (gasoline) and 818

(diesel) have been split into on-road and off-road components so that new profiles from Gabele and DRI could be included (see **Table 6**).

Table 6 shows that the Gabele profile assigned to off-road gasoline sources assumes the top ranking in terms of MIR-weighted TOG emissions, with profile 401 (on-road gasoline exhaust) assuming a lower priority. Another effect of these changes is that the total MIR-weighted TOG emissions are reduced slightly from 4,946 tons per day to 4,922 tons per day. This study has shown that the reactivity of other profiles recommended for further study—including animal waste decomposition, jet exhaust, and wildfires—is likely to decrease when those profiles are updated with more recent data. This indicates that the overall effect of suggested updates to the ARB speciation profile library will be a decrease in the reactivity of the CCOS organic gas inventory. Recent model performance analyses have suggested that the mass and/or the reactivity of the CCOS ROG inventory are underestimated (Tesche et al., 2004); therefore, this study may indicate that the problem is more likely to lie with the mass of ROG emissions.

Table 6. Revised anthropogenic TOG-, ROG-, and MIR-weighted TOG emissions by speciation profile.

Rank	Profile Number	Profile Name	TOG (tons/day)	ROG (tons/day)	Weighted Reactivity	MIR-Weighted TOG	MIR-Weighted TOG %	Cumulative MIR-Weighted TOG %
1	—	<i>Gabele lawnmower profile</i>	171	158	4.2	718	15%	15%
2	882	Gasoline – catalyst – stabilized exhaust	179	145	3.4	618	13%	27%
3	422	Hot soak emissions – California light-duty vehicles	198	197	2.4	475	10%	37%
4	877	Gasoline – catalyst – FTP bag 1-3	102	96	3.9	401	8%	45%
5	818	Farm equipment – diesel – light and heavy	73	-9	5.0	363	7%	52%
6	203	Animal waste decomposition	1,095	88	0.3	322	7%	59%
7	401	Gasoline – non-catalyst – stabilized exhaust	70	200	4.4	306	6%	65%
8	586	Composite jet exhaust JP-5	25	22	7.0	172	3%	69%
9	906	Gasoline – diurnal & resting evaporatives	87	86	2.0	172	3%	72%
10	419	Liquid gasoline – MTBE 11% – commercial grade	57	57	2.7	152	3%	75%
11	—	<i>DRI on-road diesel profile</i>	22	18	5.6	123	3%	78%
12	402	Gasoline – non-cat – FTP bag 1-3 starts	31	28	3.8	116	2%	80%
13	—	<i>New composite profiles based on source type</i>	42	29	1.8	75	2%	82%
14	—	<i>LADCO industrial surface coating profiles</i>	28	28	1.9	53	1%	83%
15	716	Medium cure asphalt	22	22	2.4	53	1%	84%
16	1902	Architectural coatings – water borne	24	24	2.0	48	1%	85%
—	All Other	Various	1,794	418	0.4	754	15%	100%
		Total	4,017	1,188	—	4,922	100%	—

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APPENDIX C

EMISSIONS RECONCILIATION FINDINGS AND RECOMMENDATIONS DECEMBER 8, 2006

TECHNICAL MEMORANDUM

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December 8, 2006

STI-905044.12-3094-TM

TO: Dr. Patricia Velasco, California Air Resources Board

FROM: Lyle R. Chinkin, President
Stephen B. Reid, Manager, Emissions Assessment Group

RE: Emissions Reconciliation Findings and Recommendations – Comparison of Ambient Measurements to Emissions Representations for Modeling

1.1 SUMMARY OF FINDINGS AND RECOMMENDATIONS

Key findings and recommendations that resulted from the Central California Ozone Study (CCOS) emissions reconciliation are summarized below:

- When compared with previous emissions reconciliation studies, the emissions data used in this project are generally in better agreement with ambient data than previous emission inventories.
- At some sites, the emissions data correlate with ambient data as closely as could be expected given the limitations of the comparison techniques used.¹
- For urbanized areas in the northern part of the CCOS modeling domain (the Sacramento area), the gridded emissions data are in good agreement with data from ambient monitoring sites on weekdays, but show poorer agreement on weekend days.
- For urbanized areas in the central part of the CCOS modeling domain (the Fresno area), the gridded emissions data are in good agreement with data from ambient monitoring sites on both weekdays and weekend days.

¹ For the types of comparisons performed in this study, emissions-derived pollutant ratios that are within ± 25 -50% of ambient-derived ratios are considered to be in good agreement (California Air Resources Board, 1997).

- For urbanized areas in the southern part of the CCOS modeling domain (Bakersfield), the gridded emissions data do not show good agreement with ambient monitoring data on either weekdays or weekend days.
- For most rural areas in the CCOS modeling domain, the gridded emissions data do not show good agreement with ambient monitoring data on either weekdays or weekend days. However, these sites do not fully meet the underlying assumptions of the analysis techniques used (i.e., significant local emissions around the monitoring site).

Based on the findings from this study, Sonoma Technology, Inc. (STI) recommends that the following steps be taken to further investigate the CCOS modeling emission inventories and to make specific improvements to those inventories:

- Improve the accuracy of weekend emission estimates in the Sacramento area. Because monitoring sites in Sacramento are likely to be primarily influenced by on-road mobile source emissions, weekend vehicle activity data should be collected and used to better characterize differences in weekday and weekend day travel.
- Correct the spatial distribution of emissions from livestock waste in the existing emission inventory. This update should resolve the discrepancies between the ethane fractions observed in the ambient and emission inventory data.
- Further investigate the poor agreement between ambient and emission inventory data in Kern County. Given that the comparison between ambient and emission inventory data is generally good at urban sites dominated by mobile sources, it may be that other source types are poorly characterized in Kern County. Source apportionment techniques, such as positive matrix factorization (PMF)² or bottom-up efforts to “ground truth” the Kern County inventory could be used to identify specific areas of improvement.
- Collect more ambient data at Bay Area sites. The possible comparisons between ambient and emission inventory data were very limited in this project given the availability of data from Bay Area sites.

A detailed description of the analysis techniques and results that served as the basis for these conclusions and recommendations are provided in the sections that follow.

² Limited PMF analyses are scheduled to be done as part of the current study with assistance from the Bay Area Air Quality Management District. No source apportionment results were ready at the time this document was prepared.

INTRODUCTION

This memorandum is a deliverable for the “CCOS—Comparison of Ambient Measurements to Emissions Representations for Modeling” project. The CCOS is a multi-year program of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling carried out for the purpose of improving the scientific understanding of ozone air quality problems in northern and central California. The goals of CCOS are being met through analysis of existing data; a large-scale field study conducted in summer 2000 to acquire a comprehensive database to support modeling and data analysis; analysis of the data collected during the field study; and the development, evaluation, and application of an air quality simulation model for northern and central California. The “CCOS—Comparison of Ambient Measurements to Emissions Representations for Modeling” project complements these other activities by investigating why preliminary CCOS photochemical modeling results differ from ambient observations by comparing emission inventory and ambient data.

The purpose of this technical memorandum is to provide the CCOS Technical Committee (TC) an assessment of the emission inventories being used for CCOS photochemical modeling efforts and to provide recommendations for meaningful improvements to the emission inventories that will improve subsequent photochemical ozone modeling results. The results of CCOS modeling will provide much of the technical basis for State Implementation Plan (SIP) updates for ozone nonattainment areas of the San Francisco Bay Area, Sacramento Valley, and San Joaquin Valley (SJV). Therefore, it is crucial that the modeling system improve its ability to predict the spatial and temporal patterns of observed ozone.

BACKGROUND

Comparisons between emission inventory- and ambient-derived data (often called “emissions reconciliation”) can identify components of an emission inventory that warrant further investigation and improvement. Such analyses commonly reveal omissions or inaccuracies, which can be iteratively investigated and remedied until the emission inventory and ambient data reconcile with one another. Recognizing potential issues and implementing needed improvements *before* continuing air quality planning activities represent opportunities for appreciable benefits, such as improved plan effectiveness, defensibility, cost savings, and/or time efficiency. Real-world examples of inventory reconciliation analyses that have produced such successes have been published by Haste et al. (1998), Korc et al. (1995), and Fujita et al. (1992).

An inventory reconciliation analysis is a selective, quantitative comparison of emission inventory- and ambient-derived molar pollutant ratios (e.g., volatile organic compounds [VOC]/oxides of nitrogen [NO_x] or carbon monoxide [CO]/NO_x) and chemical speciation profiles. Inventory reconciliation analyses are considered “top-down” evaluations because they begin with a global overview of the emission inventory and then drill down to the details by targeting selected, high-priority source types for further investigation. (In contrast, “bottom-up” evaluations begin with specific, individual emissions source categories, which are synthesized to construct a comprehensive inventory from many elements of information.) Typically, inventory reconciliation analyses attempt to address the following questions:

- How well do emission inventory-derived pollutant ratios of VOC/NO_x and CO/NO_x compare with ambient-derived pollutant ratios?
- How well does the chemical composition reported in the emission inventory compare with the chemical composition of the ambient air?
- How do the ratio comparisons and chemical species comparisons vary by hour, wind quadrant, and source influence?
- What sectors (point, area, mobile) of the emission inventory, if any, need improvement and what changes are recommended?
- How do the ratio comparisons in this study compare with past emission inventory reconciliation studies?
- Are the emission inventory estimates getting better?

Comparisons of ambient- and emission inventory-derived primary pollutant ratios are confounded by the fact that ambient concentrations are influenced not only by pollutants emitted in the near vicinity of a monitor, but also by the carryover of aged (i.e., transported or chemically changed) pollutants. The influence of aged pollutants on the comparison can be minimized (though not eliminated) by selecting ambient data collected at times when emission rates are high and chemical reaction rates are low, such as the morning hours. Emissions are generally high during morning hours, mixing depths are low, and long-range transport and chemical reactions are minimized. It should be recognized, however, that emissions from elevated sources may be injected above the mixed layer and, hence, may not affect surface-level ambient concentrations. Evaluations with and without elevated emissions sources were performed to understand the potential effects of this phenomenon.

OVERVIEW OF APPROACH

Using ambient measurements collected during the CCOS field measurement program conducted in summer 2000, STI spatially and temporally compared emission estimates with ambient air quality data by calculating emission inventory- and ambient-derived pollutant ratios (including total nonmethane organic carbon [TNMOC]/NO_x, CO/NO_x, and individual hydrocarbon species such as benzene/toluene), and performing “fingerprint analyses” on the relative amounts of individual hydrocarbon species in the ambient data and emission inventory. In addition, STI has assessed sources of uncertainty or bias associated with each analysis technique and integrated the results of previous research.

The scope of work for the project was divided into the following elements:

1. Site selection and ambient data processing
2. Emission inventory acquisition and processing
3. Comparison of ambient and emission inventory data

The technical approach for each of these work elements is described here.

Site Selection and Ambient Data Processing

During the first phase of this project, STI investigated the available monitoring sites in the CCOS modeling domain to identify sites collecting ambient data of sufficient quality and quantity for comparison with emission inventory data (Chinkin, 2005). The following criteria were considered when evaluating air quality sites in the CCOS domain:

- Availability of speciated VOC measurements
- Availability of NO_x measurements
- Availability of wind direction measurements
- Sufficient density of total organic gas (TOG) and NO_x emissions around the site
- Availability of CO or TNMOC measurements
- Number of distinct counts of VOC, NO_x, and CO above the monitor detection limit and background thresholds (for this analysis, we used VOC > 50 ppbC, NO_x > 10 ppb, and CO > 0.150 ppm)
- Visual inspection of monitoring sites using imagery from “Google™ Earth”. Sites were examined for visual evidence of local emissions

Examination of the site measurements relative to the criteria resulted in grouping the sites into five distinct “tiers”. All sites that collected speciated VOC data and NO_x measurements were classified as Tier 1, 2, or 3. These were the most suitable sites for comparisons with emission inventory data. Only five sites met all the criteria listed above and were denoted Tier 1. Two additional sites failed one of these criteria and were denoted Tier 2. Seven additional sites failed two of the criteria and were denoted Tier 3. Tiers 2 and 3 sites are typically less suitable for comparison because of low emissions near the site or insufficient measurements. Sites with no speciated VOC data that had some CO or TNMOC measurements were also considered less suitable. Sites that collected more than 10 CO or TNMOC measurements, NO_x measurements, meteorology measurements, and urban-like emissions of TOG and NO_x were denoted Tier 4. Those sites that failed one of these criteria were considered Tier 5 (unsuitable for analysis). See Appendix A for a more detailed description of the ambient measurements used in this project.

Table 1 shows the 18 sites selected during that investigation and identifies the analysis technique(s) supported by the available data at each site. STI processed the ambient air quality and meteorological data collected at the 18 sites into formats needed for comparison with the emission inventory. Statistical analyses performed on the ambient air quality data include calculations of minima, maxima, means, medians, and confidence intervals. STI analyzed validated surface meteorological data to understand and account for the potential influences of meteorology—in particular, wind speed and direction—on the ratio comparisons.

Table 1. Monitoring sites selected for emissions reconciliation analyses.

Site	Tier	District	Site Name	TNMOC/NO _x Ratios	CO/NO _x Ratios	Species Ratios	VOC Fingerprints
BGS	1	SJV	Bakersfield Stn. (Golden State)	X	X	X	X
CLO	1	SJV	Clovis Stn.	X	X	X	X
FSF	1	SJV	Fresno Stn. (First St.)	X	X		
NAT	1	Sacto	Sacramento/ Natomas Stn.	X	X	X	X
SDP	1	Sacto	Sacramento Stn. (Del Paso Manor)	X		X	X
FLN	2	Sacto	Folsom Stn.	X		X	X
PLR	2	SJV	Parlier Stn.	X		X	X
SUN	3	Bay Area	Sunol Stn.			X	
ARV	3	SJV	Arvin Stn.	X	X	X	X
ELK	3	Sacto	Elk Grove Stn.	X			X
M29	3	SJV	Madera Stn.	X		X	X
SHA	3	SJV	Shafter Stn.	X		X	X
SJ4	3	Bay Area	San Jose Stn. (4th St.)		X		
TSM	3	SJV	Turlock Stn.		X		
BAC	4	SJV	Bakersfield Stn. (California Ave.)		X		
GNBY	4	Sacto	Granite Bay Stn.			X	

Emission Inventory Acquisition and Processing

Staff at the California Air Resources Board (ARB) provided STI with the latest gridded emission inventories prepared for the July/August 2000 modeling episode. These inventories reflect recent updates to emission estimates, including the use of new versions of EMFAC, the ARB's on-road mobile source emissions model, and OFFROAD, the ARB's off-road mobile source emissions model. Emissions were gridded to the 190 x 190 cell CCOS modeling domain at a resolution of 4 km. Specific emission inventory files provided by ARB include

- gridded area and off-road mobile source emissions for an August 2000 weekday and weekend day;
- gridded surface and elevated point source emissions for an August 2000 weekday and weekend day;
- gridded, hourly on-road mobile source emission files for individual dates from July 27, 2000, through August 2, 2000;
- gridded, hourly biogenic emission files for individual dates from July 27, 2000, through August 2, 2000;
- organic gas speciation profiles and a cross-reference file to match profiles to inventory source categories; and
- temporal profiles used by ARB to distribute daily emission estimates across the hours of the day.

STI applied ARB's temporal profiles to the area, off-road mobile, and point source emissions to generate hourly estimates for those source types. Temporal profile assignments were based on an ARB cross-reference file that matches diurnal profiles with individual source categories. For on-road mobile and biogenic sources, average weekday and weekend day emission estimates were produced from the day-specific files provided by ARB. STI then applied ARB's speciation profiles to all emission inventory files to disaggregate TOG emissions into individual chemical species. The resulting speciated inventories contained hundreds of chemical species; however, the ambient data collection and analysis methods are only capable of quantifying hydrocarbons containing between 2 and 12 carbon atoms (approximately). Therefore, to ensure that the same chemical compounds are being compared in the ratio comparisons, the individual chemical species reported in the emission inventory were matched to those measured in the ambient data. The emission inventory compounds that were not measured in the ambient samples were excluded from the analysis. Finally, prior to making comparisons between the emission inventory and ambient data, the emission inventory data were converted from mass to molar units.

Comparison of Ambient and Emission Inventory Data

For the selected sites, TNMOC/NO_x, CO/NO_x and ratios of individual species (acetylene/benzene, acetylene/propylene, benzene/m- and p-xylene, benzene/o-xylene, benzene/toluene, toluene/m- and p-xylene, and toluene/o-xylene) were computed from the ambient and emission inventory data. To make consistent comparisons of TNMOC between the ambient and emission inventory data, only the species measured at the monitoring sites were used in the emission inventory calculations. In addition, ambient-derived ratios were compared with emission inventory-derived ratios by spatially matching ambient data by wind quadrant to corresponding grid quadrants (groups of grid cells) surrounding the ambient monitoring site. Grid analysis zones were selected for each site based on predominant wind speeds during the early morning hours (0500-1000 PDT). Average wind speeds were used to identify which grid cells to include in the ratio analyses based on approximate air parcel travel distance during the time period selected for analysis.

Comparisons between ambient- and emission inventory-derived TNMOC/NO_x, CO/NO_x and ratios of individual species were made for both individual wind quadrants and full extent analysis zones surrounding each site. **Figure 1** illustrates an example of a full extent grid analysis zone centered on an ambient monitoring site, and the wind quadrant definitions, whose extents vary according to the observed wind speeds at each site. The wind quadrant grid extents are larger at sites where wind speeds are greater and smaller where wind speeds are light.

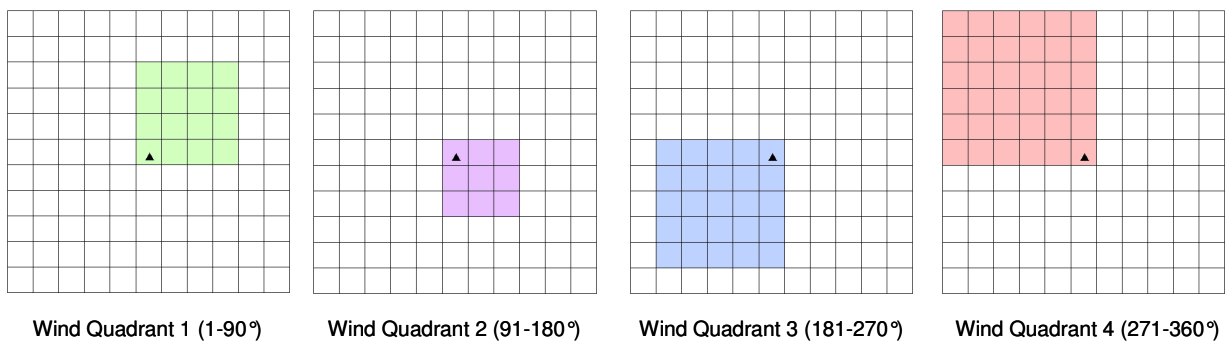


Figure 1. Example illustration of the spatial configuration of grid cells for which ambient- and emission inventory-derived ratios comparisons were calculated. The center point (▲) represents the ambient monitoring site, blank grid cells represent the entire analysis zone, and the colored grid cells represent the wind quadrant definitions and quadrant analysis zones.

For ambient data, both average and median pollutant ratios were calculated, and for the emission inventory data, ratios were calculated both including and excluding elevated point source emissions. Finally, comparisons between ambient- and emission inventory-derived pollutant ratios were also made for both weekdays and weekend days.

In addition to ratio comparisons, the chemical composition of hydrocarbons reported in the emission inventory was compared to the chemical composition of the ambient air at individual monitoring sites. These “fingerprint” analyses are used to determine how accurately the speciation of the emission inventory compares to the data measured at ambient monitoring sites. Hydrocarbon compositions were based on species groupings defined by ARB’s modeling emissions data system (MEDS) (Allen, 2001). **Table 2** shows the 35 group definitions used by ARB, and the species measured at each monitoring site were assigned to one of these groups for purposes of comparison.

Table 2. ARB organic gas group definitions.

1	Low reactives	13	Halogens	25	Propylene
2	Ethylene	14	Terpenes	26	1,3-butadiene
3	Benzene	15	Glycols	27	Toluene
4	C6+ Alkanes	16	Styrenes	28	Acetaldehyde
5	C4+ Alkenes	17	Alkynes	29	MTBE
6	C8+ Aromatics	18	Amines	30	Ethanol
7	C3+ Aldehydes	19	Formaldehyde	31	Acetylene
8	Alcohols	20	Methane	32	Isoprene
9	Ketones	21	Ethane	33	C6-C11 Alkanes
10	Esters	22	Propane	98	Unclassified
11	Ethers	23	Butanes	99	Unidentified
12	Acids	24	Pentanes		

Site Characterization

To help characterize land use patterns and emission sources surrounding each ambient monitoring site, digital images of the 20 km x 20 km³ area around each site were generated using Google EarthTM (see Appendix A). In addition, emission totals for 0500-1000 PDT were calculated for the full grid extent around each monitoring site and for each wind quadrant using the gridded emission inventory data provided by ARB. An overview of the characteristics of key monitoring sites appears below.

San Jose – 4th Street (SJ4)

The SJ4 site is located in the center of a heavily populated urban area, with heavily traveled freeways occupying all wind quadrants. The emission inventory data for the grid cells surrounding this site show that light-duty motor vehicles are the most significant source of TNMOC, CO, and NO_x emissions for each wind quadrant, while non-road mobile sources and point sources also contribute significantly to the TNMOC and NO_x emissions in quadrant 4 (see **Figure 2**). Overall emission densities⁴ are highest in quadrant 4.

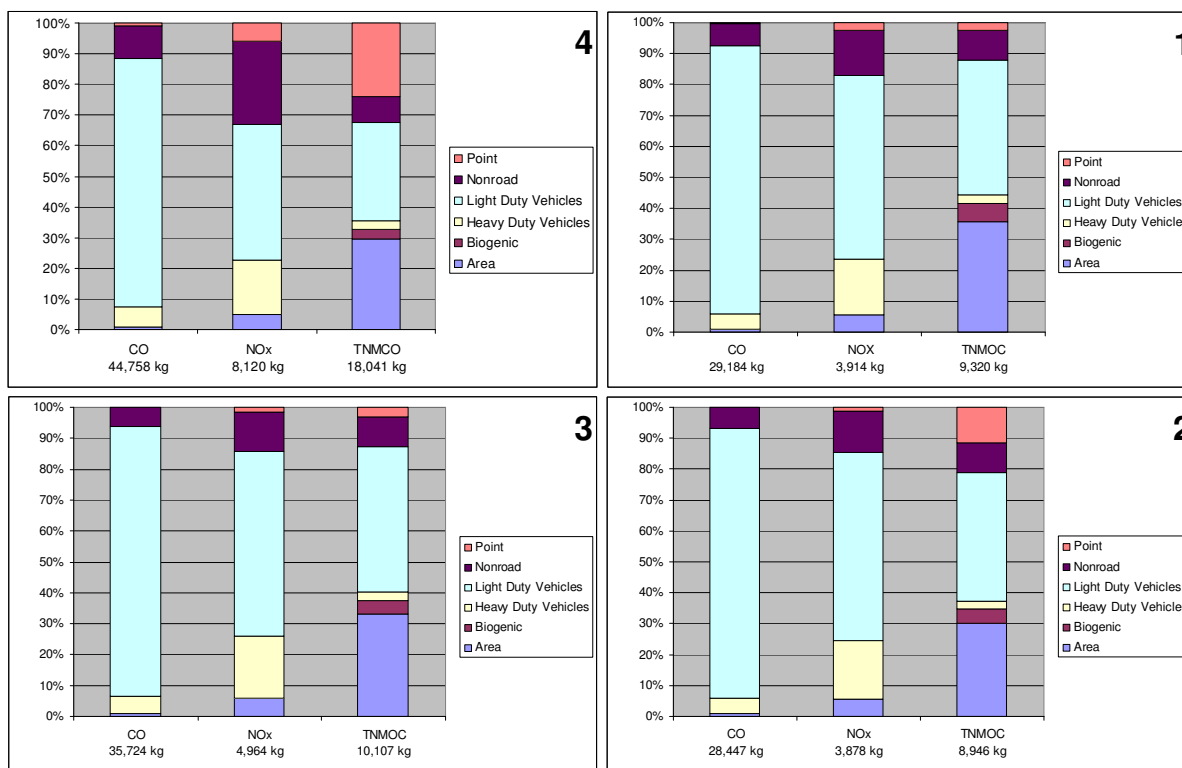


Figure 2. Emissions by wind quadrant for the San Jose 4th Street Station (0500-1000 PDT).

³ In general, the full grid extent around individual monitoring sites was 5 x 5 grid cells, or 20 km x 20 km.

⁴ The emission totals in kg shown on all bar charts represent emissions for 0500-1000 PDT for the full grid extent around each site.

Elk Grove (ELK)

The Elk Grove site is located in a rural area about 30 km south of downtown Sacramento. The emission inventory data for the grid cells surrounding this site show that CO and NO_x emissions are dominated by on-road mobile sources in all quadrants, while TNMOC emissions are also significantly influenced by area sources, particularly in quadrants 1 and 2 (see **Figure 3**). Overall emissions densities are highest in quadrants 1 and 2.

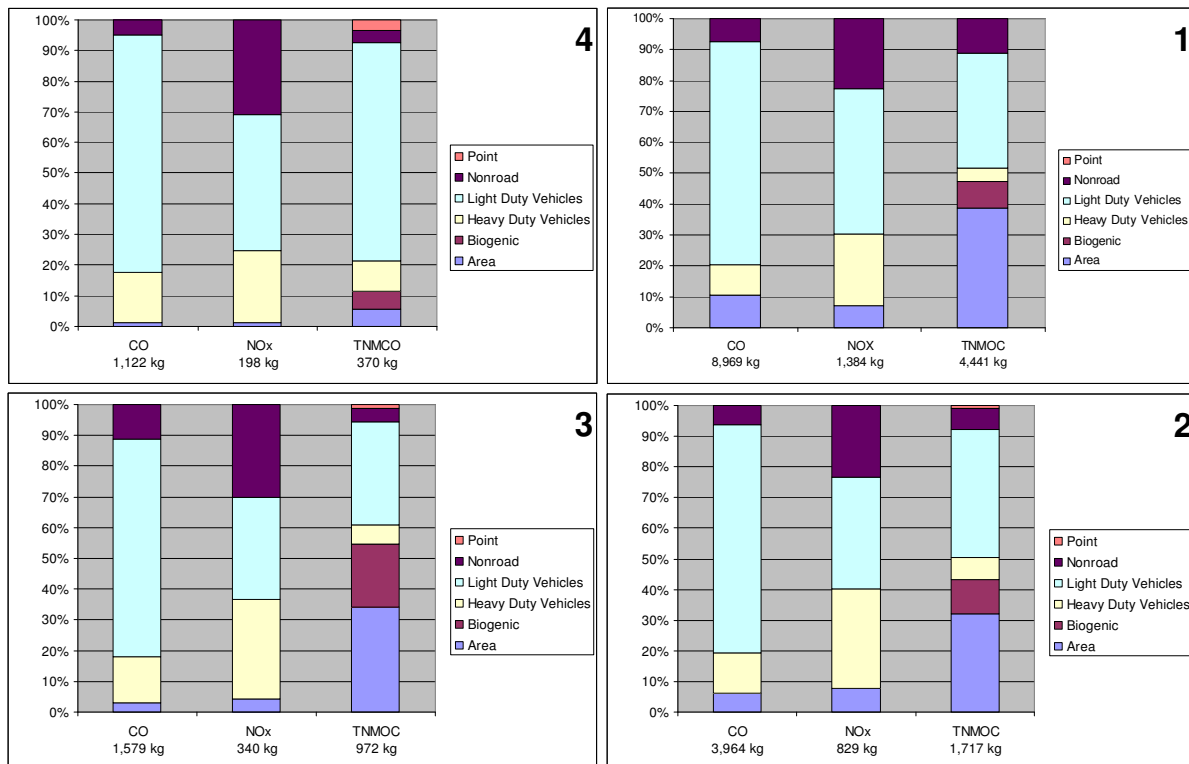


Figure 3. Emissions by wind quadrant for the Elk Grove Station (0500-1000 PDT).

Folsom (FLN)

The Folsom site is located in a suburban area to the south of Folsom Lake and about 30 km east of downtown Sacramento. The emission inventory data for the grid cells surrounding this site show that CO and NO_x emissions are dominated by on-road mobile sources in all quadrants, while TNMOC emissions are also significantly influenced by area sources in all quadrants. Overall emissions densities are highest in quadrant 4 (see **Figure 4**).

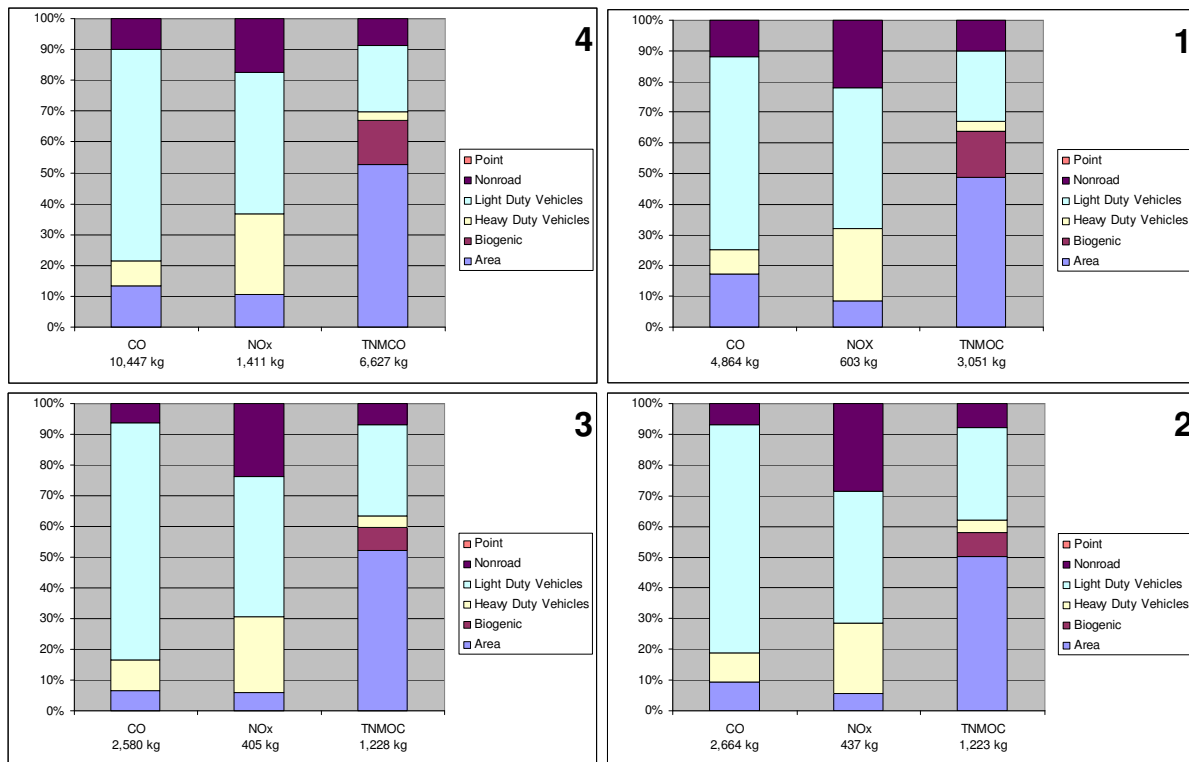


Figure 4. Emissions by wind quadrant for the Folsom Station (0500-1000 PDT).

Sacramento – Natomas (NAT)

The Natomas site is located about 6 km north of downtown Sacramento, near the intersection of Highways 5 and 80. The emission inventory data for the grid cells surrounding this site show significant on-road mobile source emissions in each quadrant, with non-road mobile sources also contributing significantly to the NO_x emissions in quadrants 3 and 4 (which contain large areas of agricultural land). Overall emissions densities are highest in quadrant 2, which is the most urbanized quadrant (see **Figure 5**).

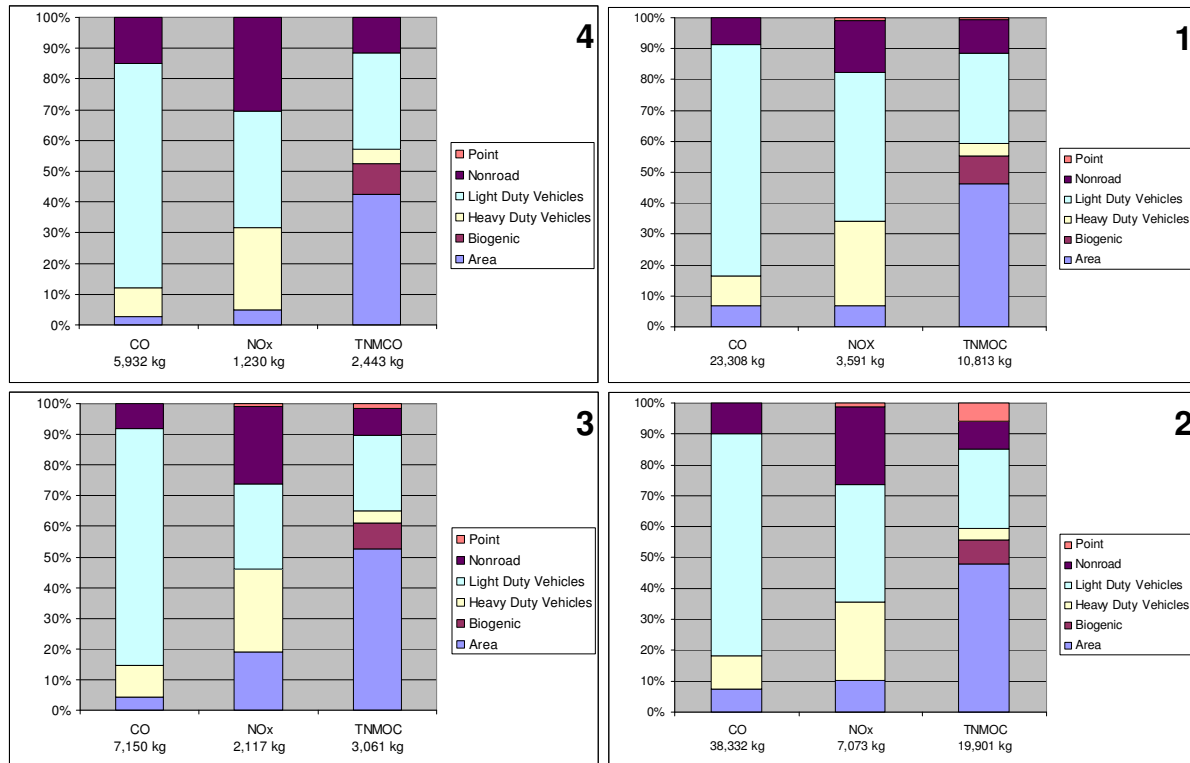


Figure 5. Emissions by wind quadrant for the Sacramento/Natomas Station (0500-1000 PDT).

Sacramento – Del Paso Manor (SDP)

The Del Paso Manor site is located in a residential area about 11 km northeast of downtown Sacramento. The emission inventory data for the grid cells surrounding this site show significant on-road mobile source emissions in each quadrant, with non-road mobile sources also contributing significantly to the NO_x emissions in quadrants 2 and 3. Area sources contribute about half of the total TNMOC emissions in each wind quadrant (see **Figure 6**). Overall emissions densities are highest in quadrants 1 and 4, which are intersected by Highway 80.

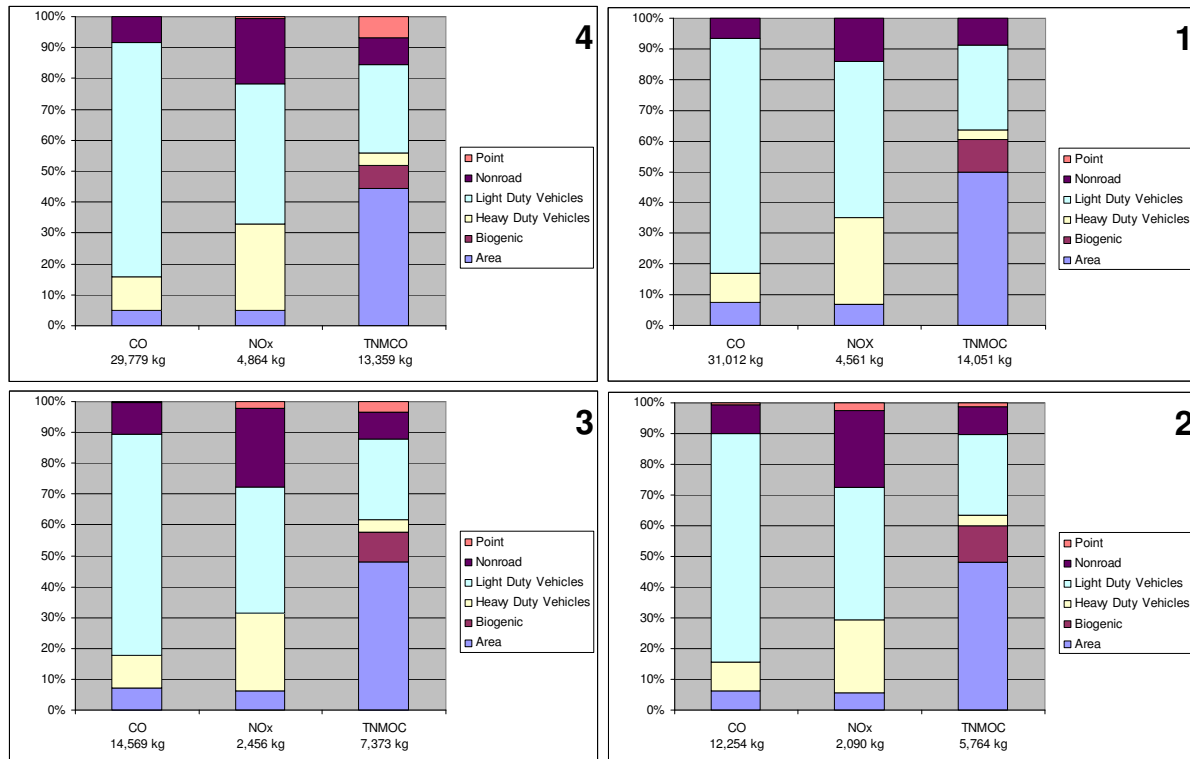


Figure 6. Emissions by wind quadrant for the Sacramento Del Paso Manor Station (0500-1000 PDT).

Clovis (CLO)

The Clovis site is located in a residential area about 10 km northeast of Fresno. The emission inventory data for the grid cells surrounding this site show significant on-road mobile source CO and NO_x emissions in each quadrant, with area sources contributing over 80% of the TNMOC emissions in each quadrant (see **Figure 7**). Overall emissions densities are somewhat lower in quadrant 1 than the remaining wind quadrants.

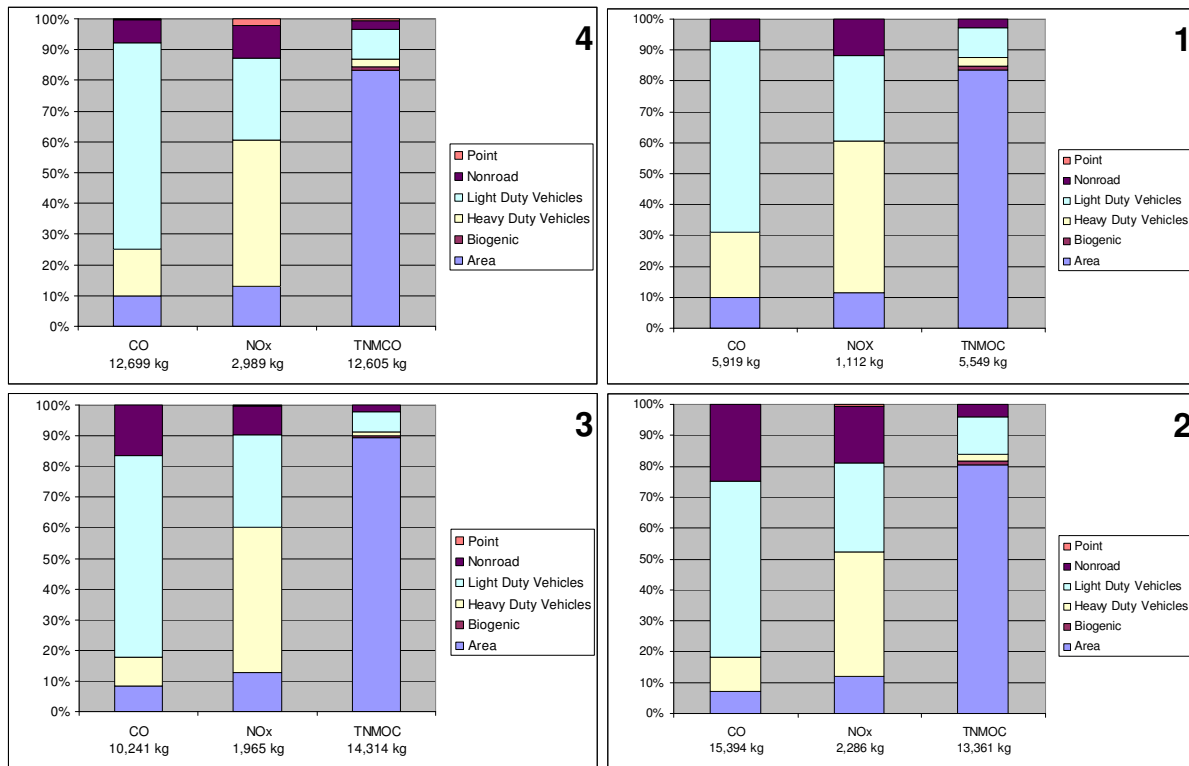


Figure 7. Emissions by wind quadrant for the Clovis Station (0500-1000 PDT).

Fresno – First Street (FSF)

The First Street site is located in a residential area about 4 km northeast of downtown Fresno. The emission inventory data for the grid cells surrounding this site show significant on-road mobile source CO and NO_x emissions in each quadrant, with area sources contributing about 90% of the TNMOC emissions in each quadrant (see **Figure 8**). Overall emissions densities are highest in quadrants 1 and 2.

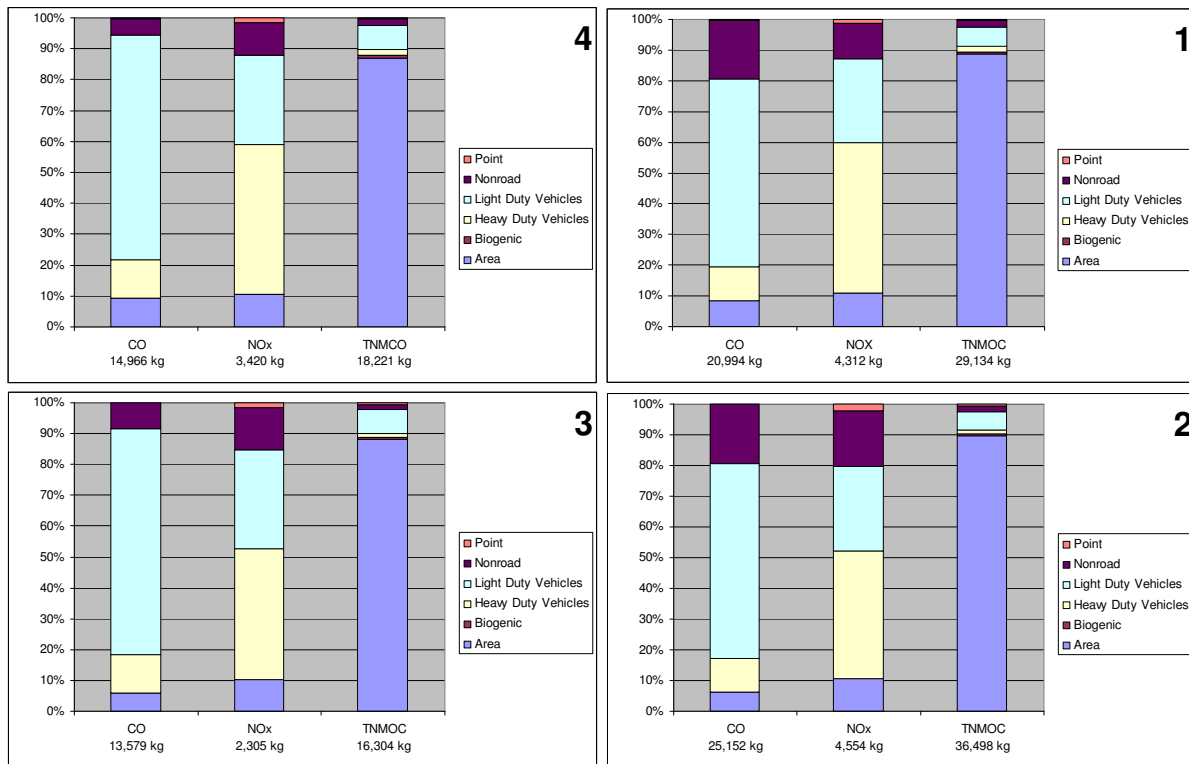


Figure 8. Emissions by wind quadrant for the Fresno First Street Station (0500-1000 PDT).

Madera (M29)

The Madera site is located in a rural area about 25 km northwest of Fresno. The emission inventory data for the grid cells surrounding this site show significant area source TNMOC emissions in each quadrant, and area sources also contribute over half of the NO_x emissions in quadrant 3. Point sources contribute almost 40% of the NO_x emissions in quadrant 4 (see **Figure 9**). Overall emissions densities are highest in quadrants 1 and 2.

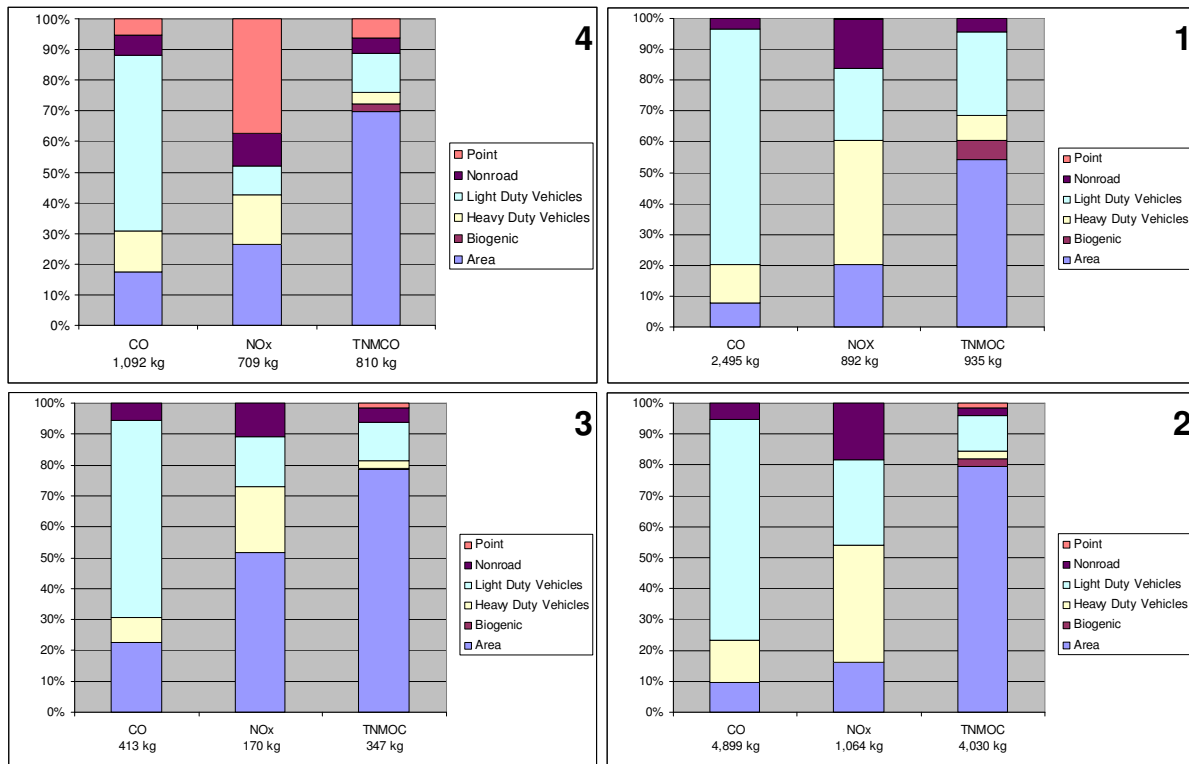


Figure 9. Emissions by wind quadrant for the Madera Station (0500-1000 PDT).

Parlier (PLR)

The Parlier site is located in a rural area about 30 km southeast of Fresno. The emission inventory data for the grid cells surrounding this site show that area sources contribute over 90% of the total TNMOC emissions in each quadrant, and point sources contribute almost half of the NO_x emissions in quadrant 3. Non-road mobile sources are a significant source of NO_x in quadrants 1 and 2 (see **Figure 10**). Overall emissions densities are highest in quadrant 2.

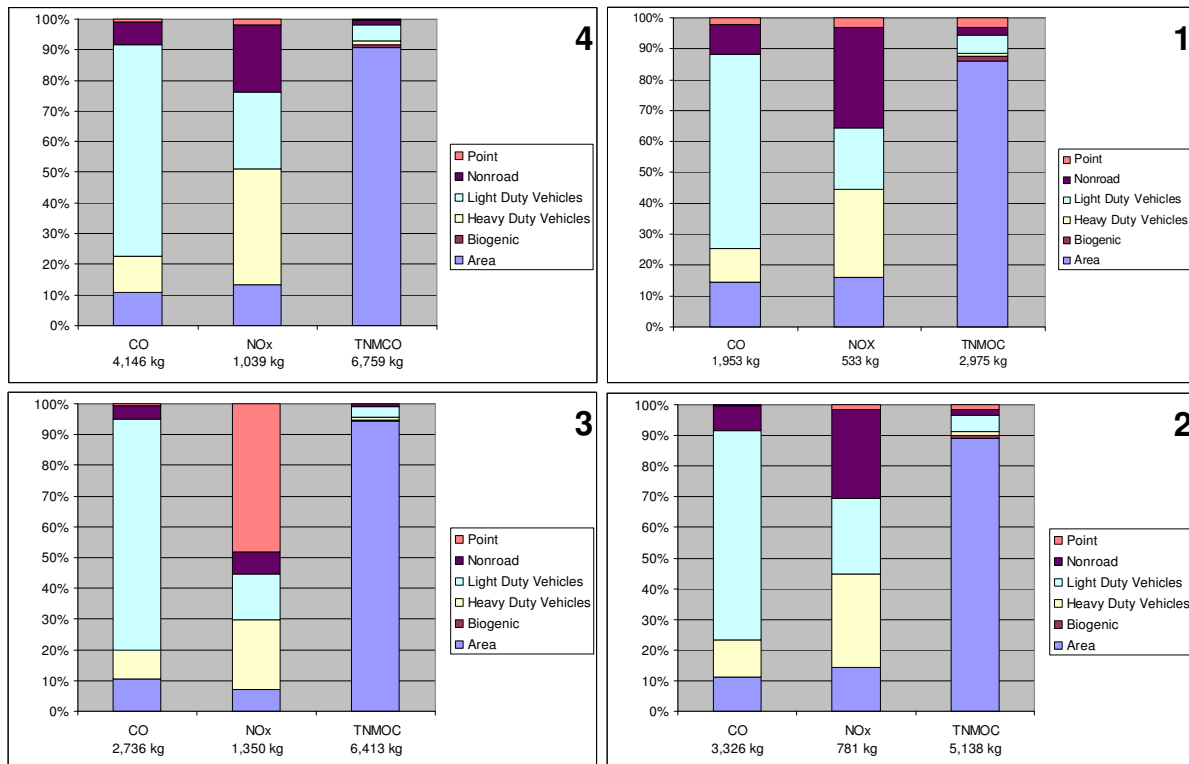


Figure 10. Emissions by wind quadrant for the Parlier Station (0500-1000 PDT).

Bakersfield – Golden State (BGS)

The Golden State site is located in a commercial area near downtown Bakersfield. The emission inventory data for the grid cells surrounding this site show that emission densities are similar in magnitude and source composition in each wind quadrant. Mobile sources are the most significant source of CO and NO_x in all quadrants, while area sources contribute about 70% of the TNMOC emissions in all quadrants (see **Figure 11**).

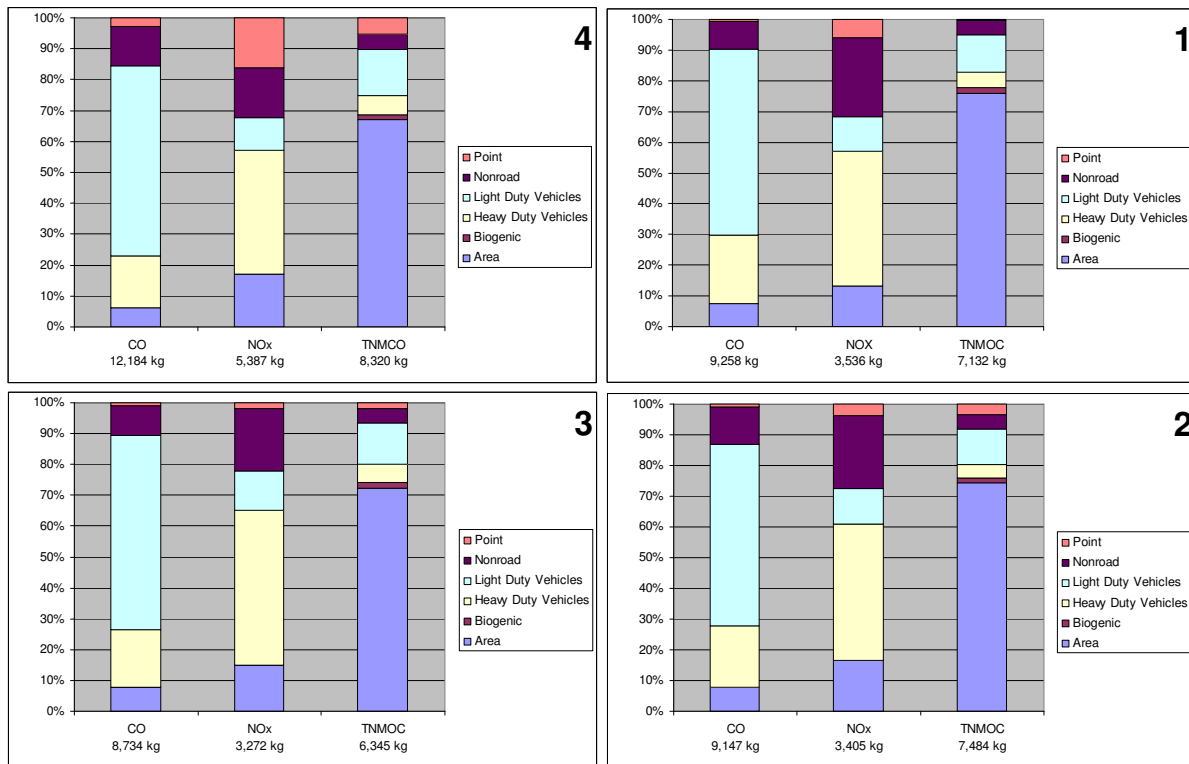


Figure 11. Emissions by wind quadrant for the Bakersfield Golden State Station (0500-1000 PDT).

Bakersfield – California Avenue (BAC)

The California Avenue site is located just south of the Kern River in a mixed commercial/residential area of Bakersfield. Across the river is an oil refinery, about 2 km northwest of the site. The emission inventory data for the grid cells surrounding this site show that area sources make up at least 65% of the TNMOC emissions in all quadrants, with point sources contributing about 10% of the TNMOC emissions in quadrants 1, 3, and 4. On-road mobile sources are the most significant source of CO and NO_x in all quadrants, and overall emission densities are highest in quadrants 1 and 2 (see **Figure 12**).

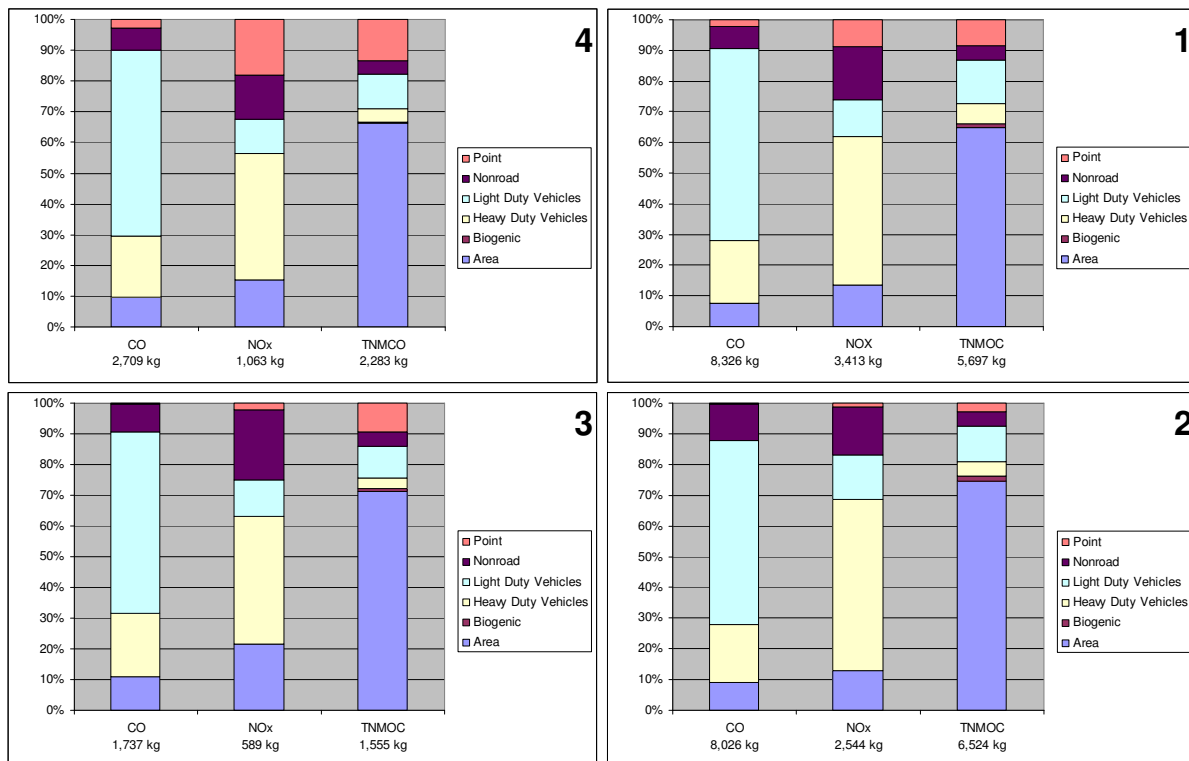


Figure 12. Emissions by wind quadrant for the Bakersfield California Avenue Station (0500-1000 PDT).

Arvin (ARV)

The Arvin site is located in a rural part of Kern County about 25 km southeast of Bakersfield. The emission inventory data for the grid cells surrounding this site show that biogenic sources contribute about 90% of the TNMOC emissions in quadrants 1 and 2, while area sources are the most significant source of TNMOC in quadrants 3 and 4. Area sources also contribute significantly to the NO_x emission inventory in quadrants 1 and 3 (see **Figure 13**).

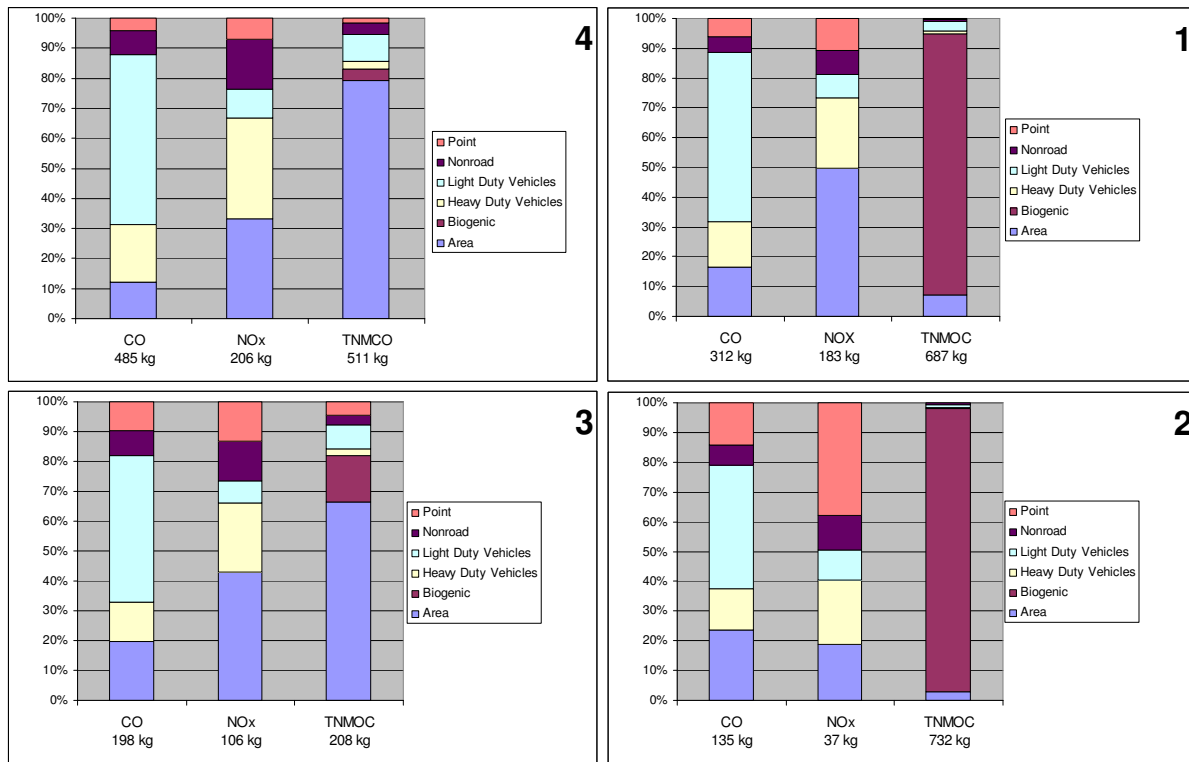


Figure 13. Emissions by wind quadrant for the Arvin Station (0500-1000 PDT).

Shafter (SHA)

The Shafter site is located in Kern County about 25 km northwest of Bakersfield. The immediate vicinity of the site is a mixed commercial/residential area, but these land use types give way to agricultural lands within about 2 km of the monitoring site. The emission inventory data for the grid cells surrounding this site show that area sources contribute about 70% of the TNMOC and about 30% of the NO_x emissions in quadrants 1 and 2, while non-road mobile sources are also a significant NO_x source in quadrants 1 and 4 (see **Figure 14**). Overall emission densities are highest in quadrants 1 and 2.

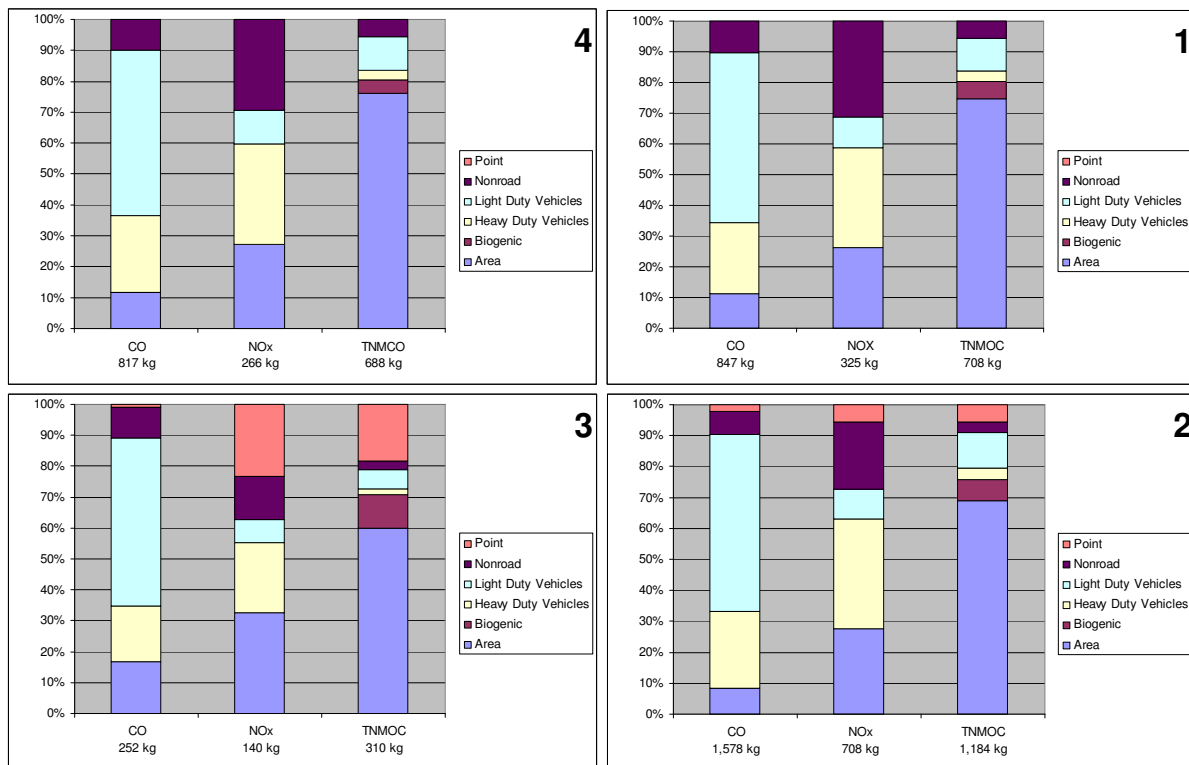


Figure 14. Emissions by wind quadrant for the Shafter Station (0500-1000 PDT).

Turlock (TSM)

The Turlock site is located in an urbanized area of the northern San Joaquin Valley about 20 km southeast of Modesto. The immediate vicinity of the site is a largely residential area, giving way to agricultural lands within a few kilometers of the monitoring site. The emission inventory data for the grid cells surrounding this site show that area sources contribute at least 80% of the TNMOC emissions in all quadrants, while on-road and non-road mobile sources are the most significant NO_x source in all quadrants (see **Figure 15**). Overall emission densities are highest in quadrants 1 and 4, which contain the city of Turlock.

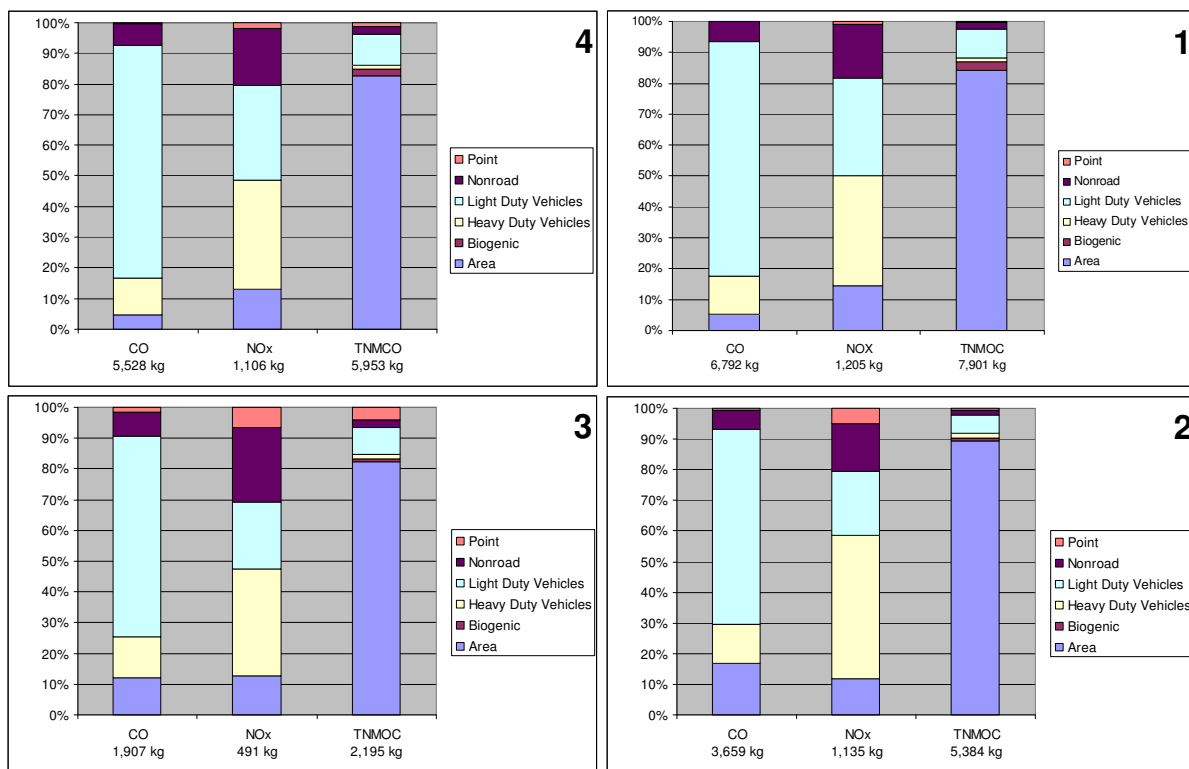


Figure 15. Emissions by wind quadrant for the Turlock Station (0500-1000 PDT).

Uncertainty Issues

Understanding the uncertainties associated with comparisons of ambient- and emission-inventory-derived pollutant ratios is essential to assess the suitability of top-down evaluation analyses. Three general categories of uncertainty issues are associated with top-down emissions reconciliation analyses: (1) accuracy of the emission inventory, (2) accuracy of the ambient concentration measurements, and (3) suitability of comparisons.

Emission Inventory Uncertainties

To compare ambient pollutant ratios to emission inventory ratios, it is important to accurately characterize, to the extent possible, the magnitude, spatial distribution, chemical

composition, and diurnal pattern of emissions. Uncertainties and inaccuracies associated with emission inventory data generally stem from (1) emissions estimation techniques and (2) emissions processing techniques. Inaccuracies and uncertainties associated with emissions estimation techniques include misclassification or exclusion of major emissions sources, the use of incorrect emissions activity data, the use of incorrect emission factors, and the use of incorrect chemical speciation profiles.

To perform an emission inventory evaluation, emissions estimates must be spatially and temporally resolved for the region surrounding the ambient monitoring sites. The methods used to disaggregate annual average countywide total emissions estimates into gridded, hourly data can introduce inaccuracies in the emission inventory data. Spatial surrogate data that are not representative of the locations of emissions sources, and temporal profiles that are not representative of the monthly, weekly, and diurnal distribution of emissions source activity can result in misrepresentation of the geographic location of emissions sources and diurnal activity patterns for sources within the vicinity (grid cells) of the ambient monitor.

Ratios of individual chemical species can be used to estimate the chemical composition of the emission inventory and specifically the different source types. Incorrect assignments of speciation profiles to emissions sources and/or speciation profiles that do not represent the chemical source composition can create emission inventory uncertainties.

Ambient Measurement Uncertainties

Uncertainties associated with ambient measurements include the influence of instrument detection limits, precision of measurements, sampling and handling losses, and reporting errors. Prior to conducting an emission inventory evaluation, the ambient data measurement methods should be assessed to ensure that the collection methods yield adequate data for this type of analysis. Furthermore, the ambient data sets intended for use must be quality-assured to eliminate invalid samples. For this study, ambient data were validated as part of an earlier project conducted by STI (Chinkin et al., 2006).

Uncertainties Associated with the Comparisons

Uncertainties associated with the comparison of ambient and emission inventory data arise from the spatial and temporal matching of ambient and emission inventory data, meteorological factors, and atmospheric reactions. To minimize differences between ambient- and emission inventory-derived ratios due to a mismatch in time and space, it is best to use emissions estimates as close to the vintage of the ambient data as is practical. For this study, emissions estimates representative of summer 2000 were compared to ambient data for the same time period.

A major premise of the top-down evaluation is that only monitoring sites and sampling periods dominated by fresh emissions are considered in the analysis. Temporal uncertainties may be caused by early morning ambient ratios that include carryover emissions in which TNMOC and/or NO_x have been preferentially removed by chemical conversion overnight. Spatial uncertainties may arise due to different influences of surface and aloft emissions. For example, TNMOC, CO, and NO_x emissions from nearby elevated sources may be injected aloft

and, as a result, may not mix into the surface air sample containing TNMOC, CO, and NO_x emissions.

Meteorological factors such as wind speed, direction, and mixing depth determine the spatial distribution of emissions and, thus, which emissions are sampled. For example, emissions from non-homogenous area and/or motor vehicle sources might be incompletely sampled at a given site. Atmospheric reactions modify the species distributions and mass of midday and afternoon ambient samples. Thus, comparisons from midday and afternoon periods are likely to be less reliable than morning comparisons.

OVERVIEW OF KEY FINDINGS

Detailed results by analysis method and ambient monitoring site are provided in the sections that follow.

TNMOC/NO_x Ratios

Ambient- and emission inventory-derived TNMOC/NO_x ratios were calculated for 11 sites. **Table 3** shows calculated ratios for the full grid extent around each monitoring site, and the data show that median ambient ratios are 1.4 to 6.3 times higher than emission ratios calculated with elevated sources excluded (for most sites, the emission ratios change little when elevated sources are included). The emission ratios reasonably approximated the ambient ratios for 6 sites, and these sites were primarily located in urbanized areas. For two other sites (SDP and PLR), the emission ratios reasonably approximated the ambient ratios for 3 of the 4 wind quadrants. For the remaining 3 sites where ambient ratios were consistently higher than emission ratios by a factor of two or more (BGS, M29, and SHA), two are “Tier 3” sites with relatively low emission densities in the area around the monitoring site.

Figures 16 through 19 show TNMOC/NO_x ratios by wind quadrant⁵ and day of week⁶ for sites in the Sacramento area. Overall, agreement between ambient- and emission inventory-derived ratios at these sites is significantly better on weekdays than weekend days. Since the Sacramento area sites are heavily influenced by on-road mobile source emissions, this may indicate that hydrocarbon emissions from light-duty vehicles are underestimated on weekends, that NO_x emissions from heavy-duty vehicles are overestimated on weekends, or both.

At the Elk Grove site (see Figure 16), ambient-derived TNMOC/NO_x ratios are slightly (20-30%) higher than emission inventory-derived ratios in wind quadrants 1 and 3, while the emission inventory-derived ratios are 10-40% higher in quadrants 2 and 4 (though these ambient ratios are based on less than 5 data points).

At the Folsom site (see Figure 17), ambient- and emission inventory-derived TNMOC/NO_x ratios agree to within 60% at all wind quadrants. For wind quadrants with at least

⁵ On all bar charts, the ambient value represents the median, and error bars represent the 25th and 75th percentiles. Wind quadrants or days of week without error bars indicate that less than 5 data points were available.

⁶ Day of week ratios were calculated for the full grid extent around each monitoring site, as there were insufficient data points to calculate ratios by wind quadrants for weekend days.

5 ambient data points, agreement is closest in quadrant 4, which has the highest overall emission density. At the Sacramento Natomas site (see Figure 18), ambient- and emission inventory-derived TNMOC/NO_x ratios agree to within 60% at all wind quadrants except quadrant 3, which has a higher contribution of TNMOC and NO_x emissions from area and non-road mobile sources than other quadrants.

Agreement between ambient- and emission inventory-derived TNMOC/NO_x ratios is poorest at the Sacramento Del Paso Manor site (see Figure 19), though the ratios agree to within 80% at all wind quadrants except quadrant 3. Further investigation showed that there are two large shopping centers about 1 km southwest of the SDP site (see **Figure 20**), so the low TNMOC/NO_x ratio in the emission inventory may be the result of a failure to capture hot soak emissions⁷ from vehicles parked in this shopping area.

Table 3. TNMOC/NO_x ratios by site (emission ratios for full grid extent around each site).

Station	Tier	Ambient Data		Emission Inventory		Median/EI - Low Level Only	Average/EI - Low Level Only
		Median	Average	Low Level + Elevated	Low Level Only		
Sacramento Area							
Elk Grove (ELK)	3	5.0	5.5	3.6	3.6	1.4	1.5
Folsom (FLN)	2	6.7	7.3	4.3	4.4	1.5	1.7
Sacramento - Natomas (NAT)	1	3.9	3.8	3.1	3.1	1.2	1.2
Sacramento - Del Paso Manor (SDP)	1	7.4	7.8	3.6	3.6	2.1	2.2
Fresno Area							
Clovis (CLO)	1	7.5	7.9	3.9	3.9	1.9	2.0
Fresno - First Street (FSF)	1	5.1	5.4	3.9	3.9	1.3	1.4
Madera (M29)	3	9.4	10.8	1.2	1.5	6.3	7.2
Parlier (PLR)	2	6.9	7.3	2.2	3.2	2.2	2.3
Bakersfield Area							
Arvin (ARV)	3	4.8	5.9	3.4	3.3	1.5	1.8
Bakersfield - Golden State (BGS)	1	6.3	6.7	1.8	1.9	3.3	3.5
Shafter (SHA)	3	5.9	6.4	2.3	2.3	2.6	2.8

⁷ CCOS on-road mobile source emissions are spatially allocated with the Direct Travel Impact Model (DTIM), which assigns hot soak emissions to the grid cell containing the centroid of a given travel analysis zone (TAZ). In the area around the SDP monitoring site, TAZs generally cover an area of several blocks and are smaller than the 4-km x 4-km grid cells that make up the modeling domain.

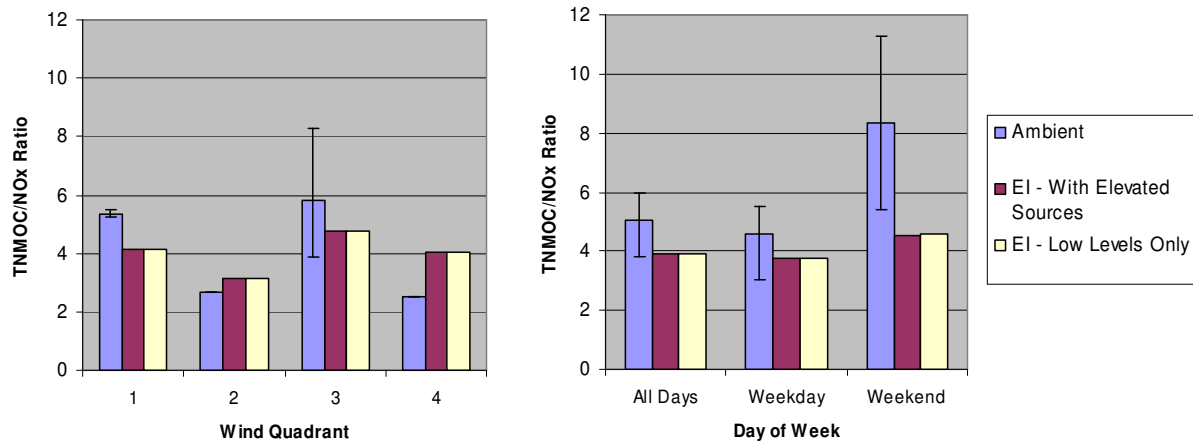


Figure 16. TNMOC/NO_x ratios by wind quadrant and day of week for the Elk Grove site.

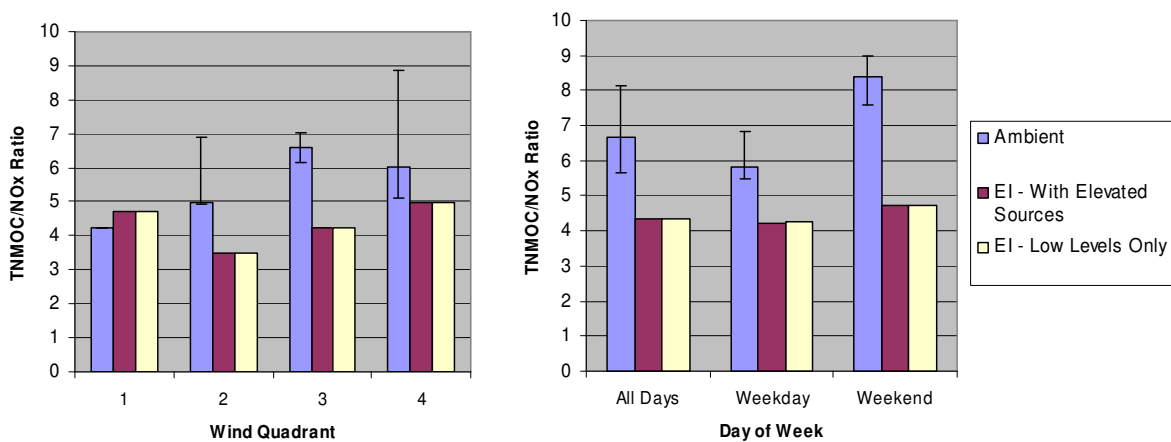


Figure 17. TNMOC/NO_x ratios by wind quadrant and day of week for the Folsom site.

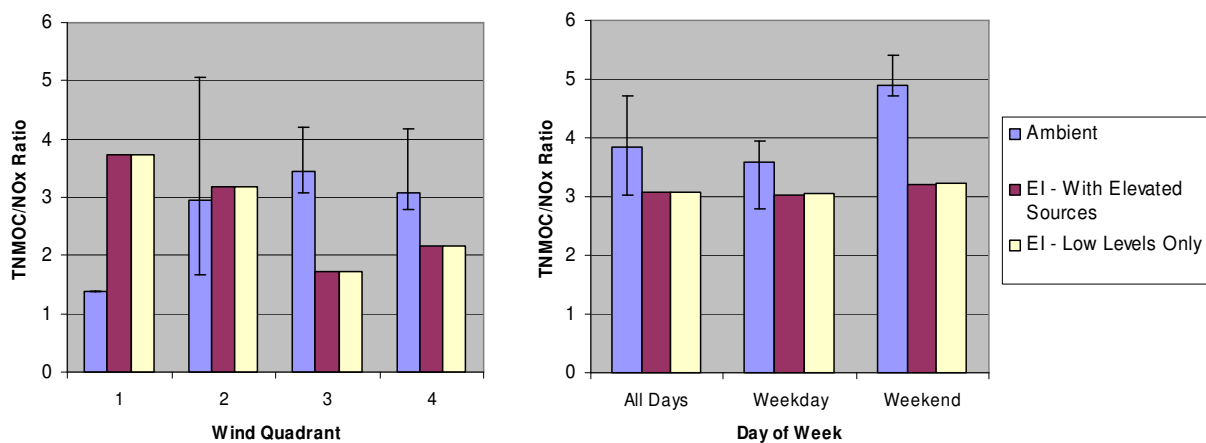


Figure 18. TNMOC/NO_x ratios by wind quadrant and day of week for the Sacramento Natomas site.

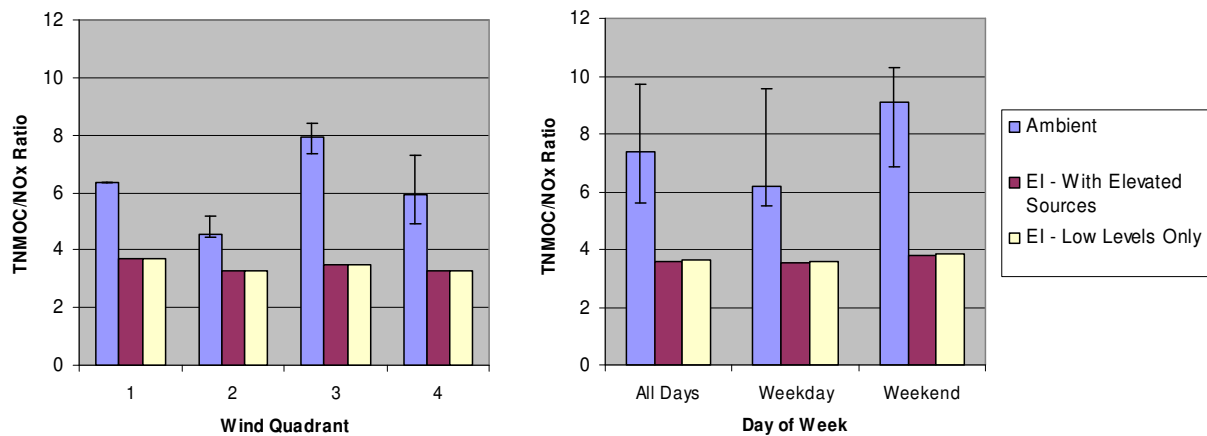


Figure 19. TNMOC/NO_x ratios by wind quadrant and day of week for the Sacramento Del Paso Manor site.

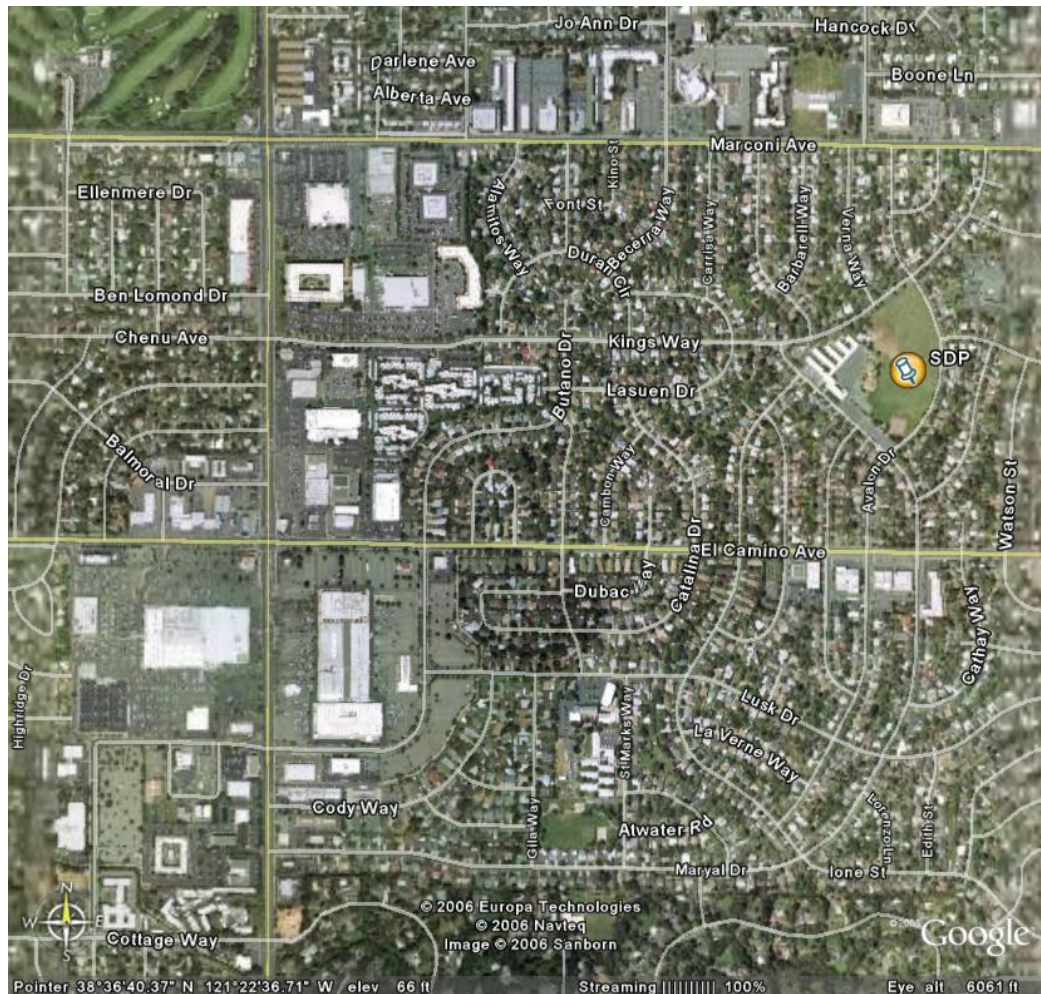


Figure 20. Wind quadrant 3 of the Sacramento Del Paso Manor site.

Figures 21 through 24 show TNMOC/NO_x ratios by wind quadrant for the Fresno area. Unlike the Sacramento area sites, agreement between ambient- and emission inventory-derived ratios at sites in the Fresno area does not vary significantly on weekdays versus weekend days. At the two urban sites in the region (Clovis and Fresno First Street), emission inventory-derived TNMOC/NO_x ratios are within 50% of emission inventory-derived ratios in all wind quadrants except for quadrant 3 at the Clovis site, where the ambient-derived ratio is 2.1 times higher than the emission inventory-derived ratio (see Figures 21 and 22). This quadrant contains large residential areas that have developed between Clovis and Fresno, and the current spatial allocation of area source emissions may not capture new “fill in” growth in this region.

At the Madera site, ambient-derived TNMOC/NO_x ratios are 3 to 10 times higher than emission inventory-derived ratios. Because this is a rural site with very low emission densities, it is likely that the site is primarily impacted by transported pollutants rather than local sources. At the Parlier site, another rural site in the Fresno area, ambient-derived TNMOC/NO_x ratios are 1.3 to 2.5 times higher than emission inventory-derived ratios. Quadrant 3 has the poorest agreement between ambient- and emission inventory-derived ratios, and this quadrant contains the town of Selma and a large winery (see **Figure 25**) that could not be identified in the point source inventory provided by ARB.

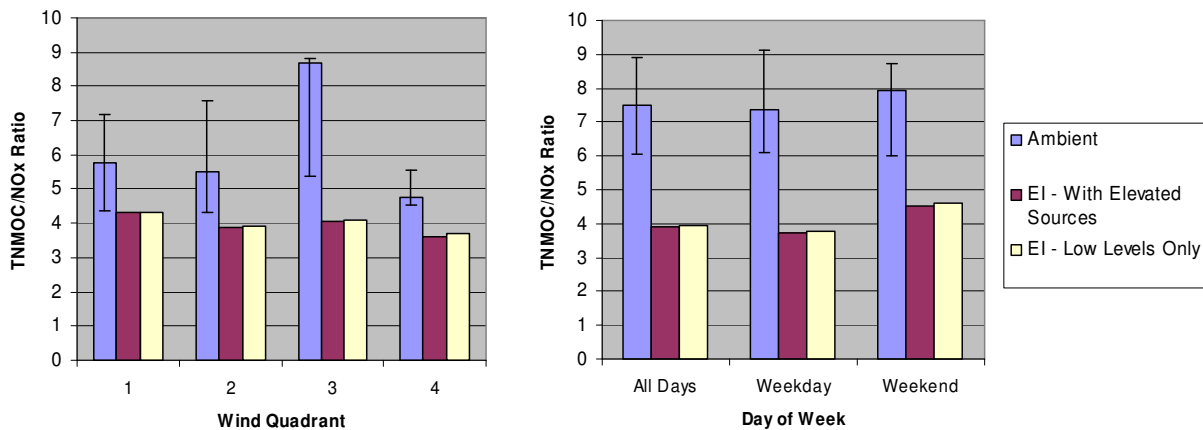


Figure 21. TNMOC/NO_x ratios by wind quadrant and day of week for the Clovis site.

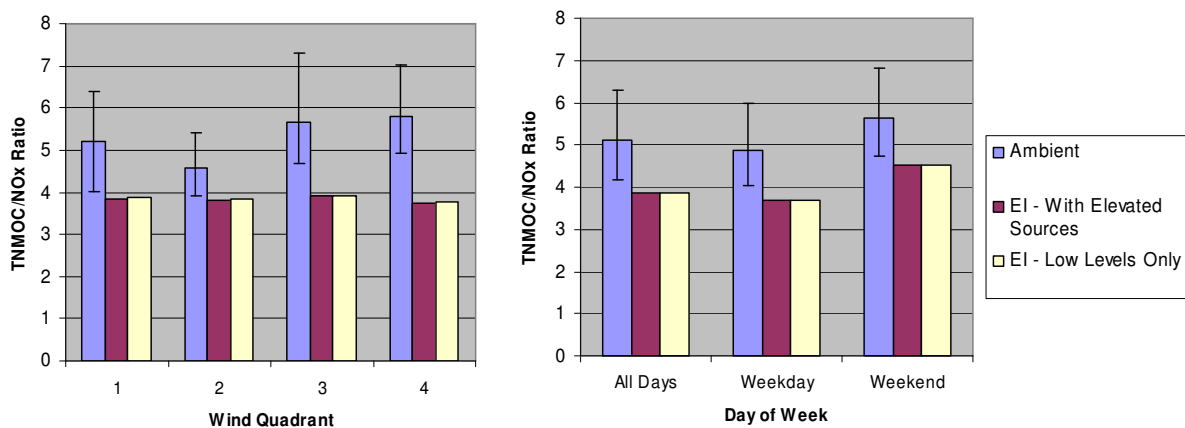


Figure 22. TNMOC/NO_x ratios by wind quadrant and day of week for the Fresno First Street site.

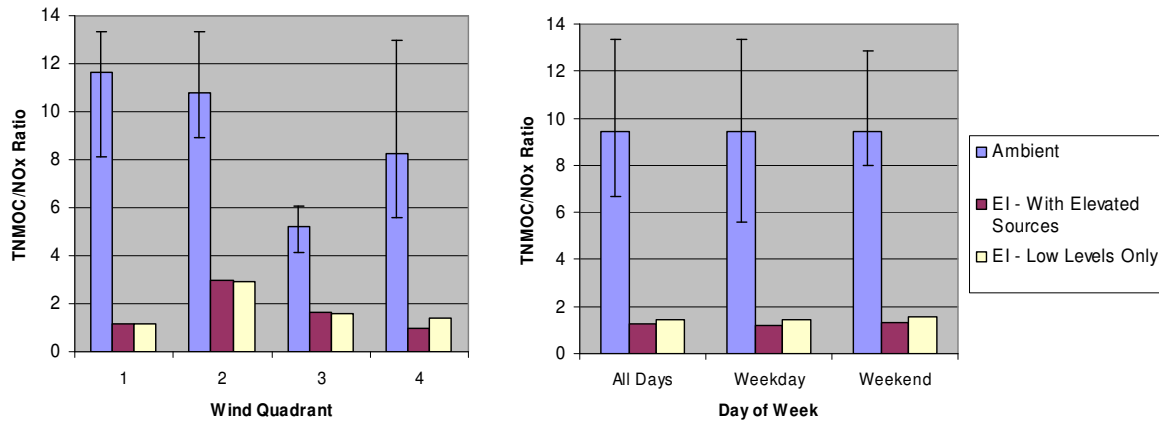


Figure 23. TNMOC/NO_x ratios by wind quadrant and day of week for the Madera site.

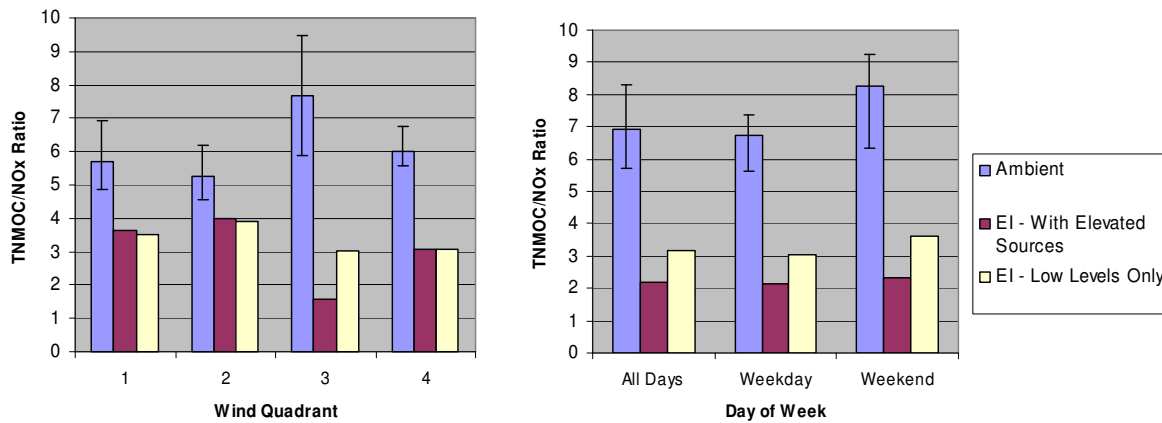


Figure 24. TNMOC/NO_x ratios by wind quadrant and day of week for the Parlier site.



Figure 25. Unidentified winery in wind quadrant 3 of the Parlier site.

Figures 26 through 28 show TNMOC/NO_x ratios by wind quadrant for sites in Kern County. At the Bakersfield Golden State site, ambient-derived TNMOC/NO_x ratios are 3 to 4 times higher than emission inventory-derived ratios for all wind quadrants and days of the week. The emission inventory is similar in magnitude and source composition for all wind quadrants, though point sources emissions are somewhat higher in quadrant 4, where there is an oil refinery and other industrial sources.

At the two rural sites in Kern County (Arvin and Shafter), significant differences also exist between ambient- and emission inventory-derived TNMOC/NO_x ratios. At the Arvin site, the ratios agree closely for all wind quadrants except for quadrant 2, which is dominated by biogenic emissions. At the Shafter site, ambient-derived TNMOC/NO_x ratios are 2 to 3 times higher than emission inventory-derived ratios for all wind quadrants and days of the week. However, emission densities are very low for both these sites, so it is likely that the sites are being influenced primarily by transported pollutants rather than local sources.

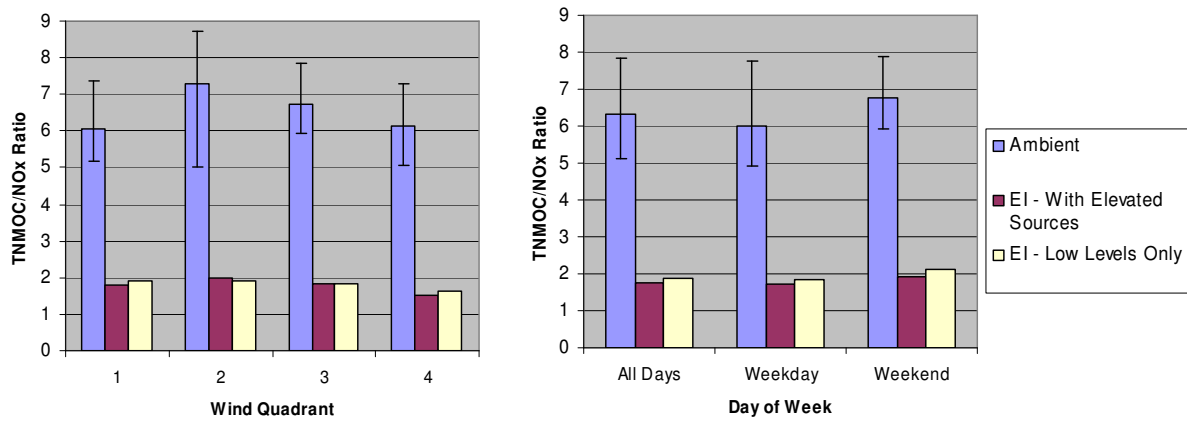


Figure 26. TNMOC/NO_x ratios by wind quadrant and day of week for the Bakersfield Golden State site.

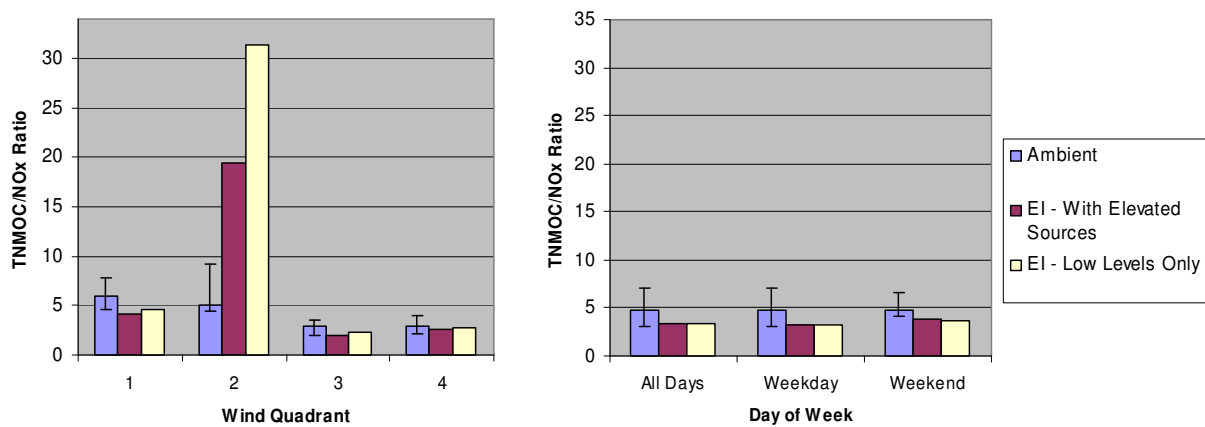


Figure 27. TNMOC/NO_x ratios by wind quadrant and day of week for the Arvin site.

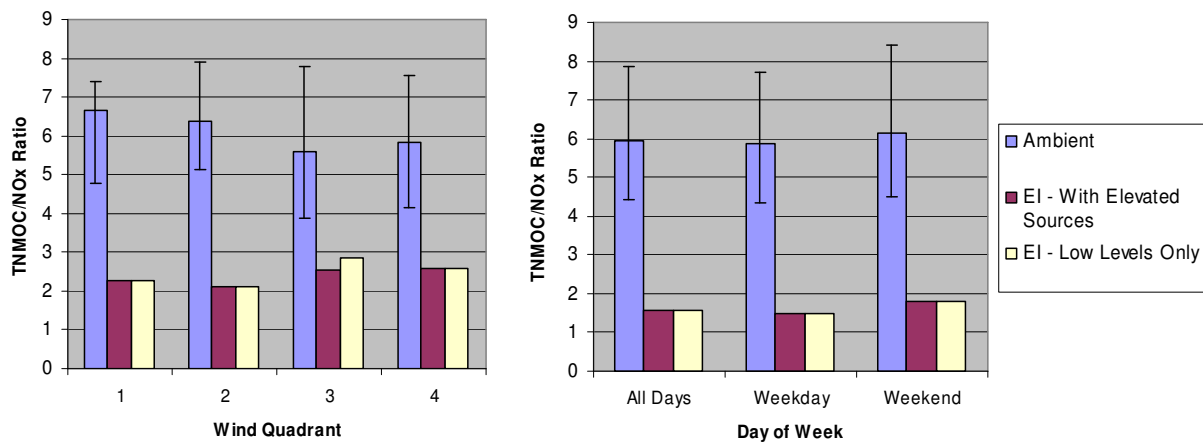


Figure 28. TNMOC/NO_x ratios by wind quadrant and day of week for the Shafter site.

CO/NO_x Ratios

Ambient- and emission inventory-derived CO/NO_x ratios were calculated for eight sites. **Table 4** shows calculated ratios for the full grid extent around each monitoring site, and the data show that median ambient ratios are 1.1 to 3.9 times higher than emission inventory ratios calculated with elevated sources excluded. The emission inventory ratios show the best comparison at urbanized sites in San Jose, Sacramento, and Fresno, with sites in Bakersfield (BAC and BGS) comparing less favorably.

Table 4. CO/NO_x ratios by site (emission inventory-derived ratios for full grid extent around each site).

Station	Tier	Ambient Data		Emission Inventory		Median/EI Low Level Only	Average/EI Low Level Only
		Median	Average	Low Level + Elevated	Low Level Only		
Bay Area							
San Jose – 4 th Street (SJ4)	3	17.6	18.9	10.5	10.8	1.6	1.8
Sacramento Area							
Sacramento – Natomas (NAT)	1	14.3	15.8	8.8	8.9	1.6	1.8
Sacramento – Del Paso Manor (SDP)	1	11.5	12.4	10.1	10.2	1.1	1.2
Fresno Area							
Clovis (CLO)	1	18.9	19.8	8.7	8.7	2.2	2.3
Fresno – First St. (FSF)	1	14.3	15.2	8.2	8.3	1.7	1.8
Bakersfield Area							
Bakersfield – California Ave. (BAC)	4	10.0	11.4	4.1	4.4	2.3	2.6
Bakersfield – Golden State (BGS)	1	18.2	19.9	4.2	4.7	3.9	4.2
Other							
Turlock Station (TSM)	3	17.6	18.2	7.2	7.4	2.4	2.5

Figure 29 shows CO/NO_x ratios by day of week for the San Jose 4th Street site (ratios by wind quadrant were not calculated due to a lack of wind data). The emission inventory-derived ratios closely approximate ambient-derived ratios overall, with weekday ratios showing closer agreement than ratios for weekend days.

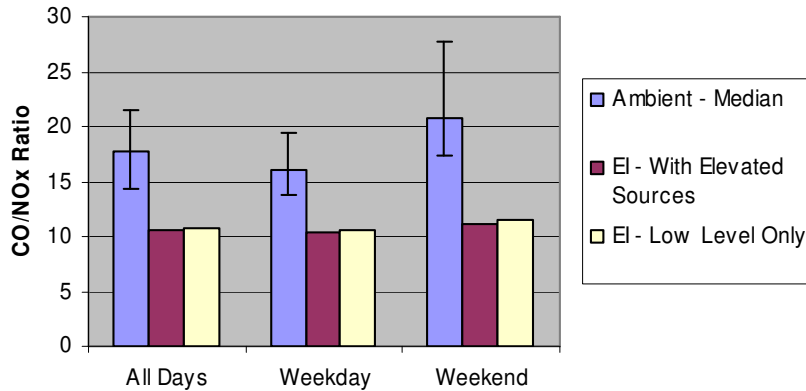


Figure 29. CO/NO_x ratios by day of week for the San Jose 4th Street site.

Figures 30 and 31 show CO/NO_x ratios by wind quadrant and day of week for Sacramento sites. At the Natomas site, emission inventory-derived CO/NO_x ratios reasonably approximate ambient-derived ratios (i.e., within 40-80%) for all wind quadrants except quadrant 3, where the ambient-derived ratio is 2.5 times higher than the emission inventory-derived ratio. According to emission inventory data, light-duty motor vehicles emit almost 90% of the CO emissions in quadrant 3, where urbanized west Sacramento gives way to large areas of agricultural land.

At the Del Paso Manor site, emission inventory-derived CO/NO_x ratios agree very closely with ambient-derived ratios (i.e., within 10-60%) for all wind quadrants and days of week (see Figure 30). At this site, the emission inventory-derived ratios correlate with ambient-derived ratios as closely as could be expected given the limitations of the comparison techniques used.

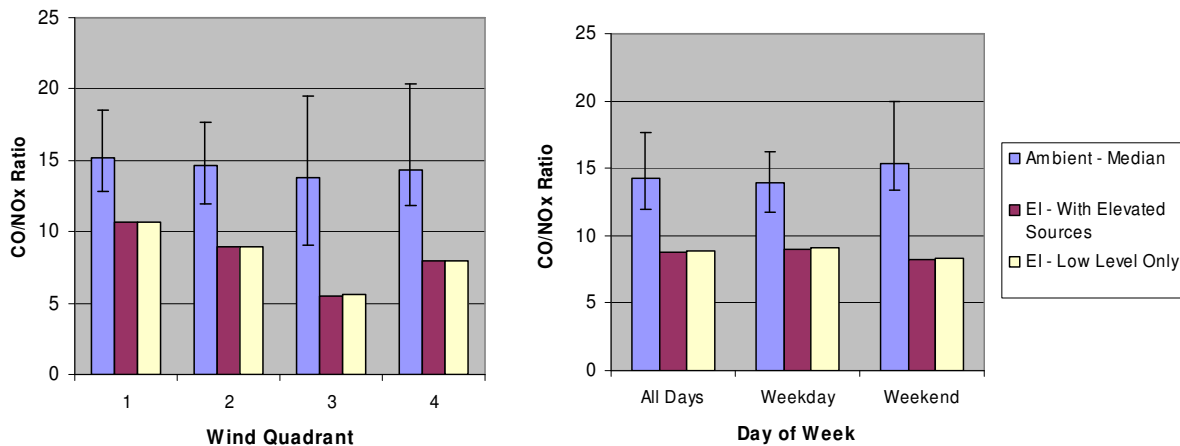


Figure 30. CO/NO_x ratios by wind quadrant and day of week for the Sacramento Natomas site.

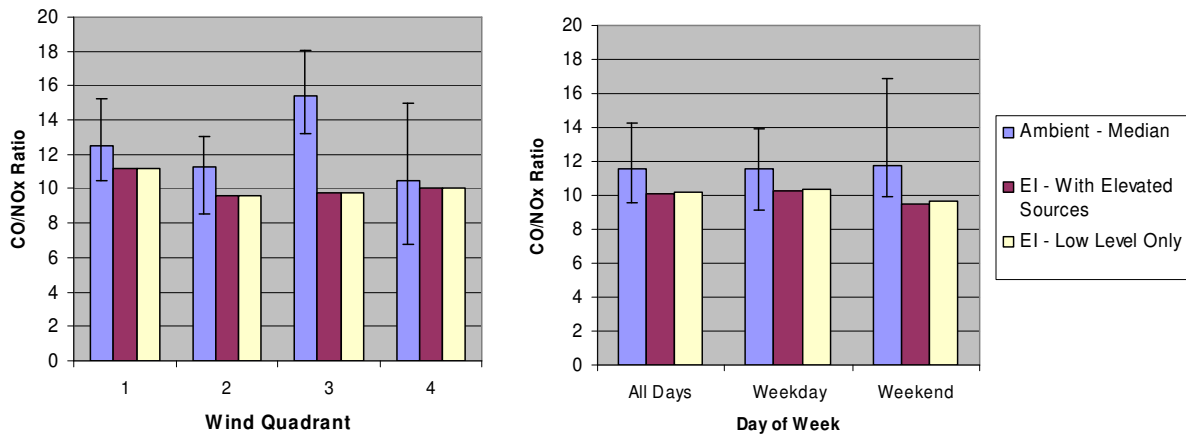


Figure 31. CO/NO_x ratios by wind quadrant and day of week for the Sacramento Del Paso Manor site.

Figures 32 and 33 show CO/NO_x ratios by wind quadrant and day of week for Fresno area sites. At the Clovis site, ambient-derived CO/NO_x ratios are approximately two times higher than emission inventory-derived ratios for all wind quadrants except quadrant 2, where the ambient-derived ratio is only 60% higher than the emission inventory-derived ratio. Ambient- and emission inventory-derived CO/NO_x ratios show slightly closer agreement on weekend days than weekdays at the Clovis site (see Figure 32).

At the Fresno First Street site, emission inventory-derived CO/NO_x ratios reasonably approximate ambient-derived ratios (i.e., within 30-80%) for all wind quadrants except quadrant 4, where the ambient-derived ratio is 2.3 times higher than the emission inventory-derived ratio. Ambient- and emission inventory-derived CO/NO_x ratios show slightly closer agreement on weekend days than weekdays at the First Street site (see Figure 33).

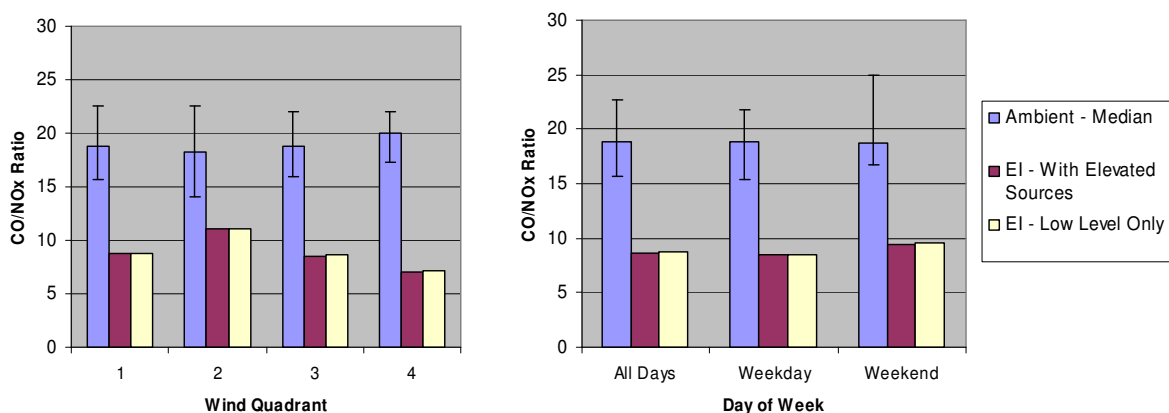


Figure 32. CO/NO_x ratios by wind quadrant and day of week for the Clovis site.

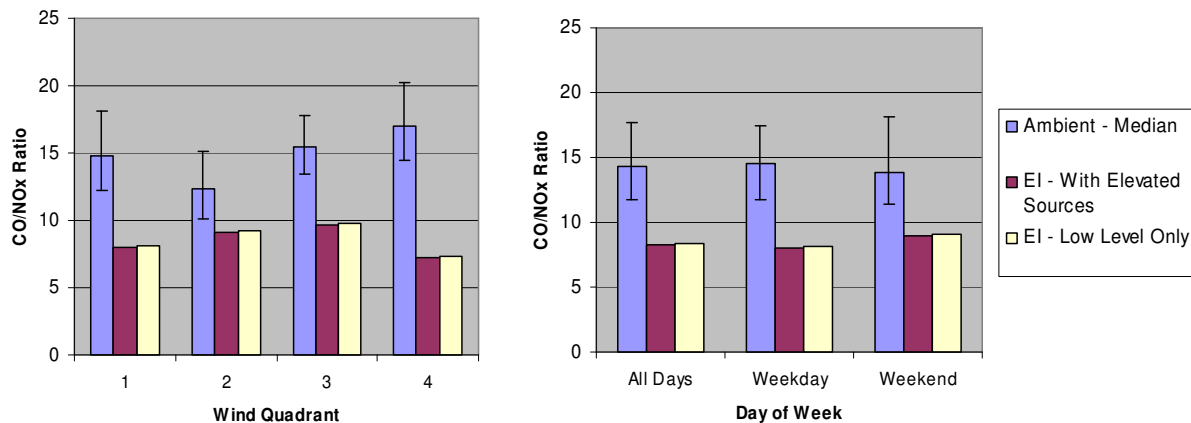


Figure 33. CO/NO_x ratios by wind quadrant and day of week for the Fresno First Street site.

Figures 34 and 35 show CO/NO_x ratios by wind quadrant and day of week for the two Bakersfield sites (California Avenue and Golden State). At the California Avenue site, emission inventory-derived CO/NO_x ratios reasonably approximate ambient-derived ratios (i.e., within 60-80%) for wind quadrants 1 and 2, while the ambient-derived ratios are more than two times higher than the emission inventory-derived ratios in quadrants 3 and 4 (see Figure 34). These differences may be partly attributable to the fact that overall emission densities are significantly higher in quadrants 1 and 2 than in the other two quadrants. At the Golden State site, emission inventory-derived CO/NO_x ratios compare poorly with ambient-derived ratios, being 3.5 to 5 times lower than ambient-derived ratios for all wind quadrants and days of the week (see Figure 35).

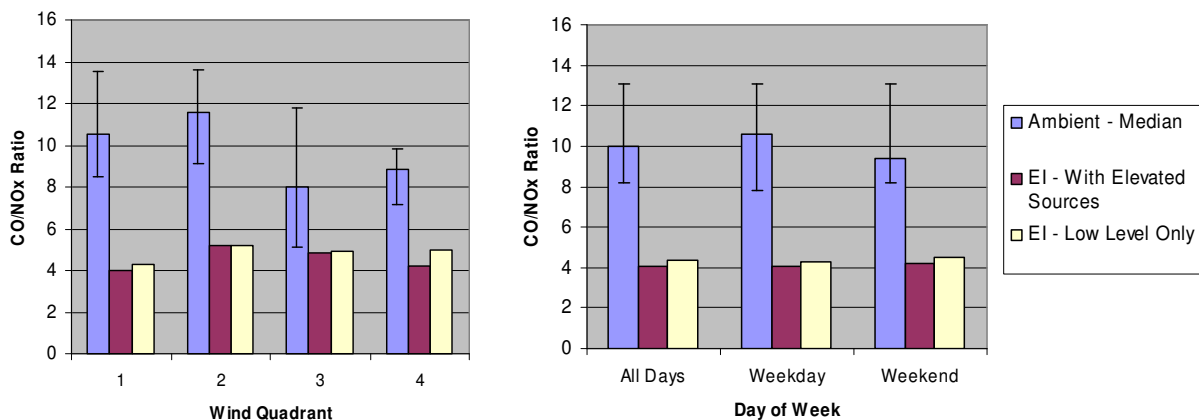


Figure 34. CO/NO_x ratios by wind quadrant and day of week for the Bakersfield California Avenue site.

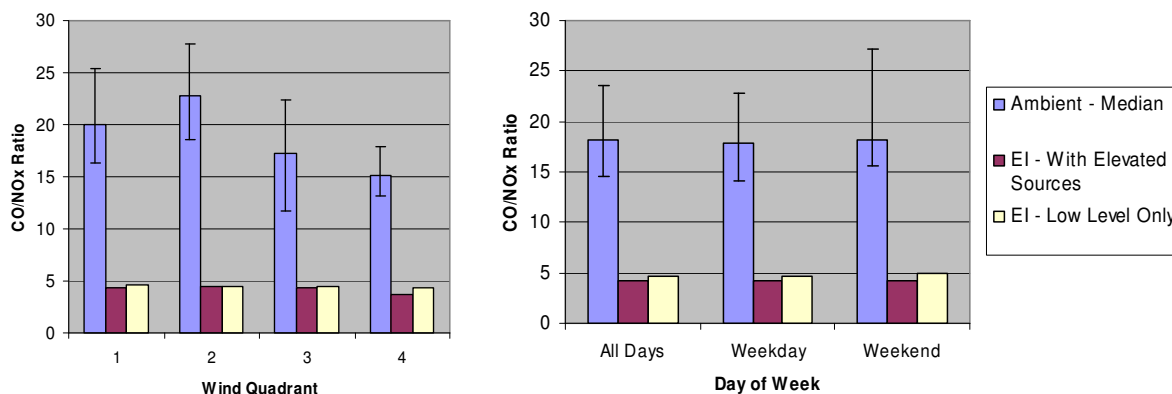


Figure 35. CO/NO_x ratios by wind quadrant and day of week for the Bakersfield Golden State site.

Figure 36 shows CO/NO_x ratios by wind quadrant and day of week for the Turlock site in Stanislaus County. Ambient-derived CO/NO_x ratios are consistently two to three times higher than emission inventory-derived ratios for this site.

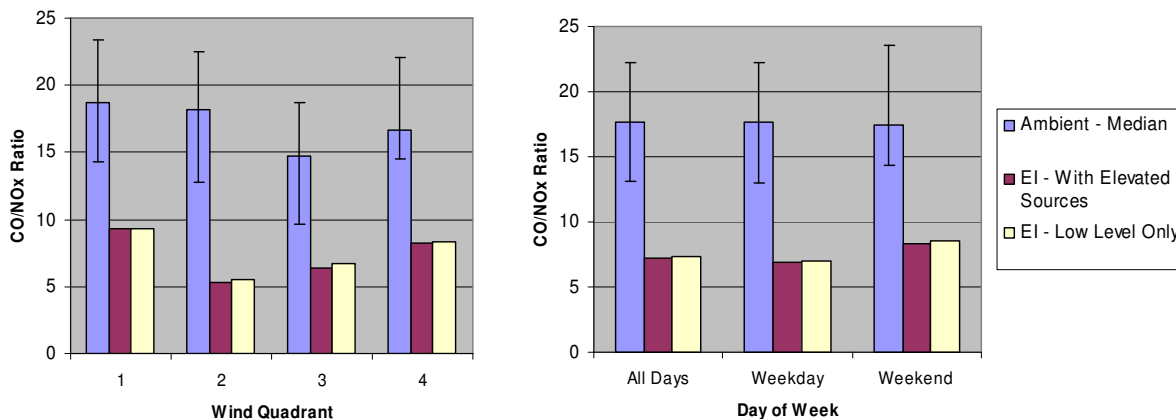


Figure 36. CO/NO_x ratios by wind quadrant and day of week for the Turlock site.

Individual Species Ratios

Further investigations of the CCOS emission inventory were conducted by comparing relative amounts of individual hydrocarbons in the ambient data and in the CCOS emission inventory. Individual species ratios were computed for 11 sites for a select number of chemical compounds: acetylene/benzene, acetylene/propylene, benzene/m- and p-xylene, benzene/o-xylene, benzene/toluene, toluene/m- and p-xylene, and toluene/o-xylene.

Table 5 shows ambient- and emission inventory-derived pollutant ratios for 13 monitoring sites in the CCOS modeling domain. Overall, the emission inventory-derived ratios show good agreement with the ambient-derived ratios, though a few significant discrepancies do exist. The emission inventory-derived acetylene/benzene ratios were in poor

agreement with the ambient-derived ratios at the Sunol and Granite Bay sites. The emission inventory-derived benzene/o-xylene ratio was also in poor agreement with the ambient-derived ratios at the Granite Bay site, and the pollutant ratios at the Parlier site compared poorly in almost all cases.

In general, these results suggest that the relative proportions of individual hydrocarbon species in the emissions data are reasonably representative of ambient data. Further investigation of the composition of hydrocarbon emissions was undertaken through the fingerprint analyses described in the following section.

Table 5. Individual species ratios by site (emission ratios for full grid extent around each site).

Station	Acetylene/Benzene			Acetylene/Propylene			Benzene/mp-Xylene			Benzene/o-Xylene			Benzene/Toluene			Toluene/mp-Xylene			Toluene/o-Xylene		
	A ^a	EI ^b	A/EI	A	EI	A/EI	A	EI	A/EI	A	EI	A/EI	A	EI	A/EI	A	EI	A/EI	A	EI	A/EI
Bay Area																					
Sunol (SUN)	6.8	1.1	6.1	–	1.1	–	0.7	0.6	1.2	2.0	1.3	1.6	0.4	0.2	1.7	1.7	2.4	0.7	4.6	5.3	0.9
Sacramento Area																					
Elk Grove (ELK)	1.1	1.2	0.9	0.7	1.1	0.6	0.7	0.6	1.2	1.3	1.7	0.8	0.4	0.4	1.1	1.8	1.7	1.1	3.6	4.7	0.8
Folsom (FLN)	1.1	1.0	1.1	1.0	0.8	1.2	0.4	0.5	0.8	1.1	1.0	1.1	0.3	0.2	1.4	1.7	2.4	0.7	4.2	4.7	0.9
Granite Bay (GNBY)	3.6	0.9	3.9	–	0.8	–	0.4	0.5	0.8	2.7	1.0	2.6	0.3	0.2	1.5	1.2	2.6	0.5	8.9	5.0	1.8
Sacramento - Natoma (NAT)	1.2	1.0	1.2	1.2	0.9	1.3	0.5	0.5	1.0	1.1	1.1	1.0	0.3	0.2	1.3	1.6	2.2	0.7	4.2	4.6	0.9
Sacramento - Del Paso Manor (SDP)	1.4	1.0	1.4	1.0	0.9	1.1	0.4	0.5	0.8	1.0	1.0	1.0	0.2	0.2	0.9	1.5	2.2	0.7	4.1	4.6	0.9
Fresno Area																					
Clovis (CLO)	1.3	1.3	1.0	1.2	1.1	1.1	0.4	0.5	0.8	1.0	1.1	0.9	0.2	0.2	1.0	1.6	2.6	0.6	4.8	5.2	0.9
Fresno - First Street (FSF)	1.3	1.2	1.0	1.1	0.9	1.2	0.4	0.5	0.8	1.0	1.1	0.9	0.2	0.2	1.0	2.0	2.6	0.8	4.7	5.4	0.9
Madera (M29)	1.3	1.8	0.7	0.9	1.2	0.8	0.5	0.7	0.8	1.3	1.7	0.8	0.3	0.3	1.1	1.9	2.4	0.8	4.5	6.1	0.7
Parlier (PLR)	2.2	1.5	1.5	–	1.2	–	8.4	0.6	14.7	4.4	1.0	4.3	20.8	0.2	130.0	1.4	3.5	0.4	2.7	6.4	0.4
Bakersfield Area																					
Arvin (ARV)	1.0	1.0	1.0	1.0	1.1	0.9	0.5	1.1	0.5	1.0	2.6	0.4	0.3	0.5	0.7	2.1	2.4	0.9	4.2	5.8	0.7
Bakersfield - Golden State (BGS)	1.6	1.1	1.5	2.7	1.0	2.6	0.4	0.7	0.6	1.0	1.4	0.7	0.2	0.3	0.7	1.5	2.4	0.6	4.2	4.9	0.9
Shafter (SHA)	1.0	1.2	0.8	1.5	1.3	1.2	0.5	1.0	0.5	1.3	2.3	0.6	0.3	0.4	0.7	1.7	2.2	0.8	5.1	5.3	1.0

^a “A” = ratios derived from ambient data.

^b “EI” = ratios derived from emission inventory data.

1.1.1 Fingerprint Comparisons

Comparisons of the ambient- and emission inventory-derived relative hydrocarbon compositions were performed for 10 sites.

In general, the fingerprint analyses showed that

- The speciation of the emission inventory is representative of the TNMOC composition detected by ambient monitoring sites for most species groups.
- The contribution of ethane to the overall TNMOC composition is consistently higher in the emission inventory than in the ambient data. Further analysis of the emission inventory showed that this overprediction is attributable to emissions from livestock waste. (In a related CCOS study [Chinkin and Reid, 2006], STI discovered that significant amounts of livestock waste emissions are being spatially distributed across the CCOS modeling domain using human population as a spatial surrogate.)
- The contribution of propane to the overall TNMOC composition is consistently lower in the emission inventory than in the ambient data. These differences may be due to the fact that propane has a low reactivity and tends to persist in the atmosphere. However, these differences may also indicate an underprediction of emissions from oil and natural gas extraction and production activities, which are a significant source of propane. This conclusion is bolstered by the fact that other species emitted by oil and gas production activities, such as butanes and pentanes, also tend to be under-predicted in the emission inventory (though these more highly reactive compounds are under-predicted by a smaller amount than propane).
- The contribution of isoprene to the overall TNMOC composition is consistently higher in the emission inventory than in the ambient data. However, these differences are likely due to the fact that isoprene, a highly reactive species, is being removed from the ambient air by photochemistry before it can be detected at monitoring sites.

Figures 37 through 40 show ambient- and emission inventory-derived hydrocarbon compositions for Sacramento area sites. In addition to the already identified issues with propane, ethane, and isoprene, note that emission inventory-derived fractions of C6+ alkanes, C4+ alkenes, C8+ aromatics, and pentanes are lower than the ambient-derived fractions at the Elk Grove site (see Figure 37). The toluene fraction is somewhat higher in the emission inventory-derived compositions than the ambient-derived compositions at the remaining three Sacramento sites (Folsom, Natomas, and Del Paso Manor), but otherwise, the hydrocarbon compositions show very close agreement at those sites.

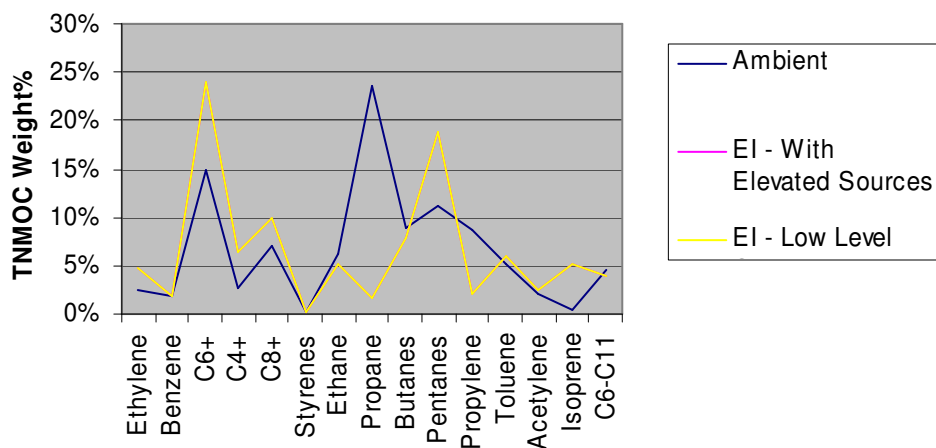


Figure 37. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Elk Grove site.

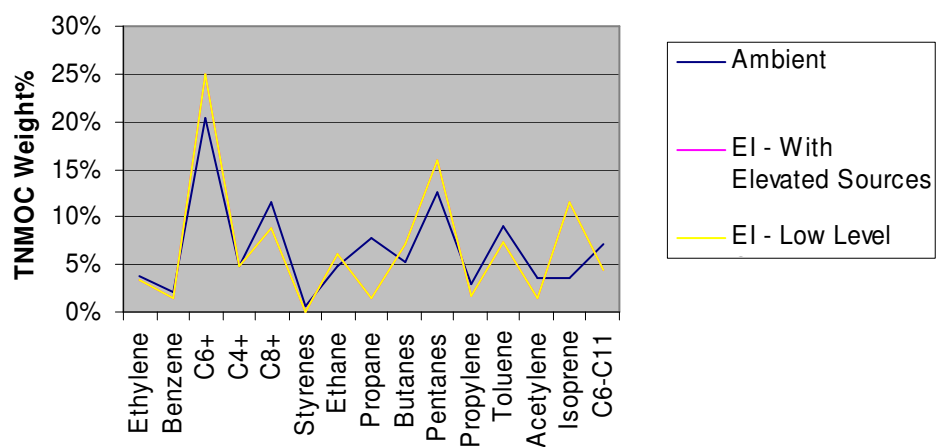


Figure 38. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Folsom site.

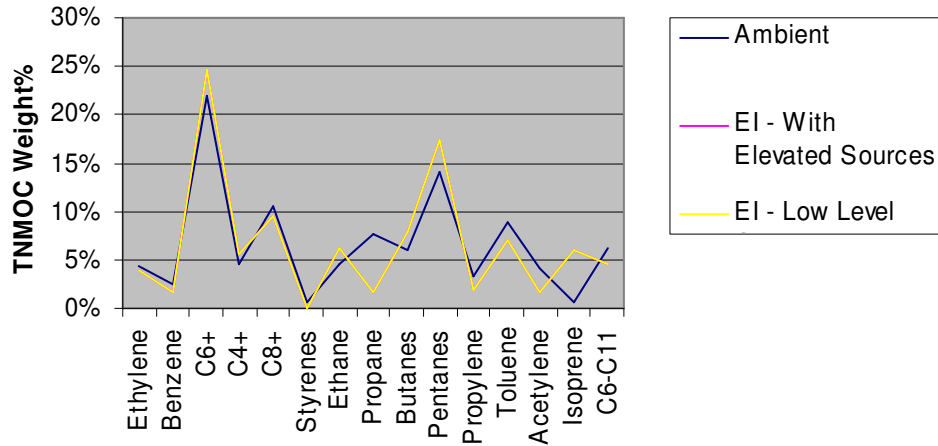


Figure 39. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Sacramento Natomas site.

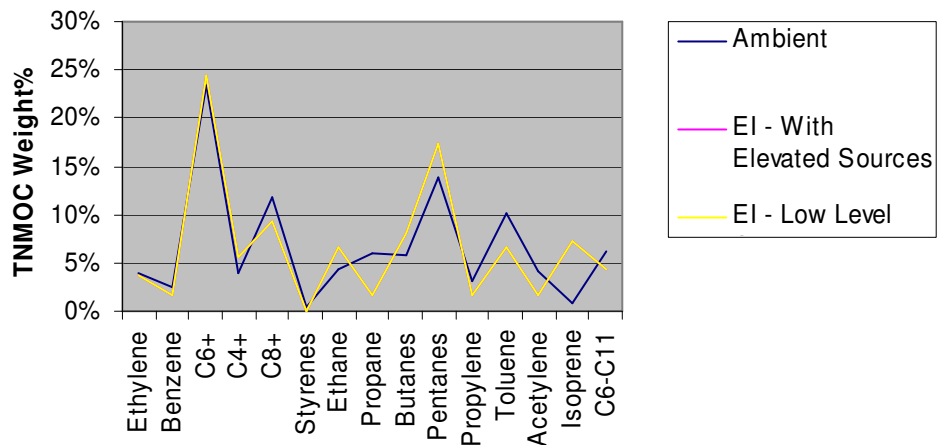


Figure 40. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Sacramento Del Paso Manor site.

Figures 41 through 43 show ambient- and emission inventory-derived hydrocarbon compositions for Fresno area sites. Again, agreement between the ambient and emission inventory data is excellent apart from the already-identified issues with ethane and propane, though C8+ aromatics and toluene are underpredicted in the emission inventory data at the Clovis site (see Figure 41).

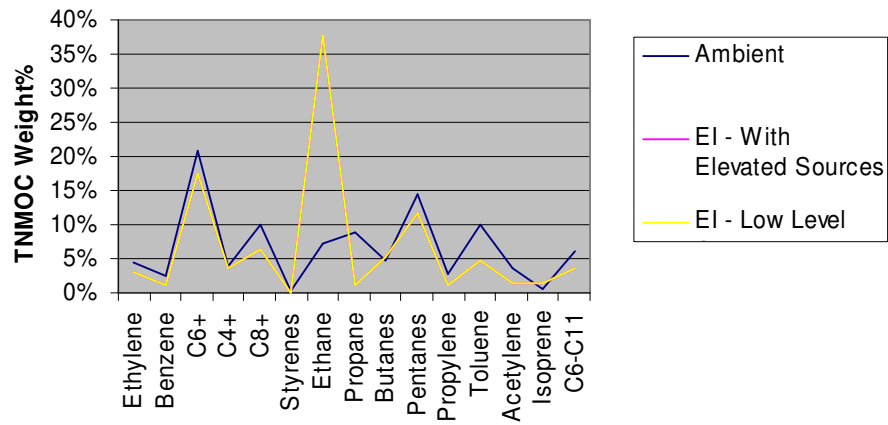


Figure 41. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Clovis site.

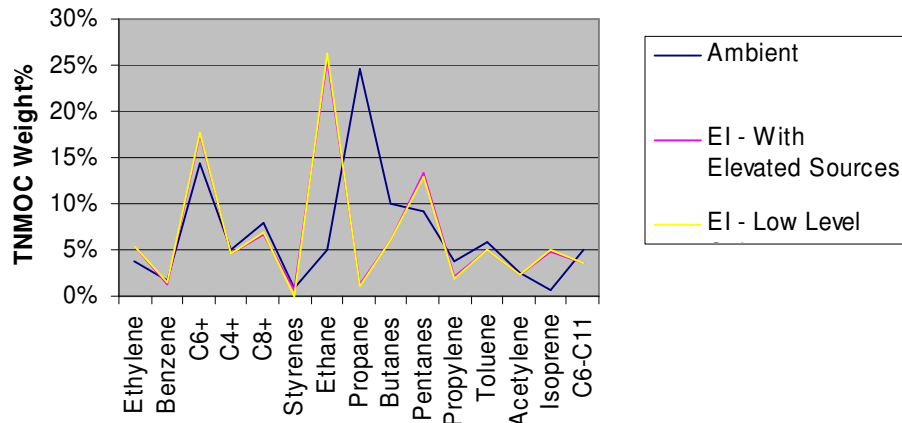


Figure 42. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Madera site.

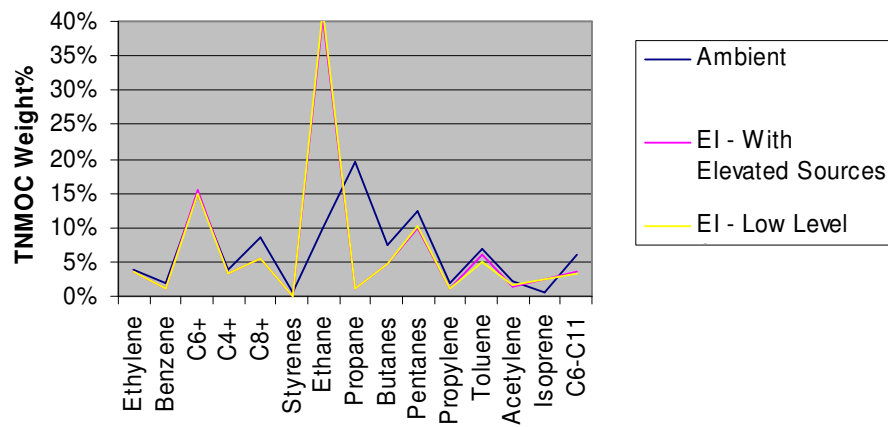


Figure 43. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Parlier site.

Figures 44 through 46 show ambient- and emission inventory-derived hydrocarbon compositions for Kern County sites, where more significant differences exist than was the case at the Sacramento and Fresno area sites. At the Arvin site, the emission inventory data show a spike in the fraction of isoprene and an underprediction of several species groups, including C6+ alkanes, ethane, and pentanes (see Figure 44). The discrepancy between ambient- and emission inventory-derived isoprene fractions is more significant at Arvin than any other site, and this difference could be caused by issues related to the reactivity of isoprene, an over-estimation of biogenic emissions in the region around the monitoring site, or terrain factors (i.e., biogenic emissions from the Sierra foothills to the east of the site are not crossing the ridgeline and impacting the monitoring site).

At the Bakersfield Golden State site, the emission inventory-derived fraction of pentanes is lower than the ambient-derived fraction, while the emission inventory-derived fraction of C6+ alkanes is lower than the ambient-derived fraction (see Figure 45). At the Shafter site, the emission inventory-derived fraction of butanes is higher than the ambient-derived fraction (see Figure 46).

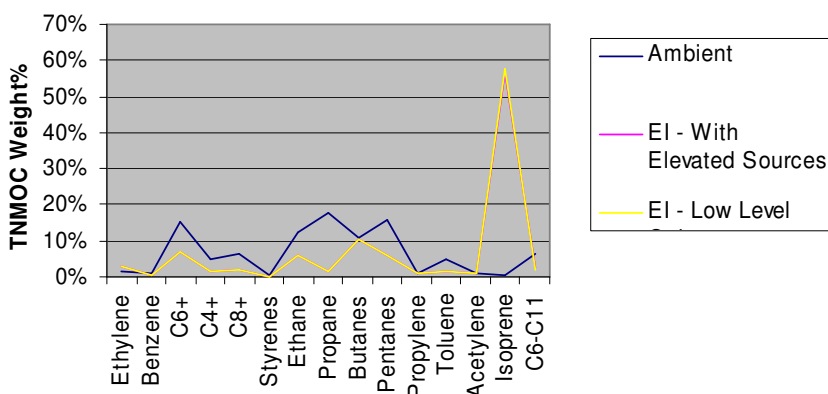


Figure 44. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Arvin site.

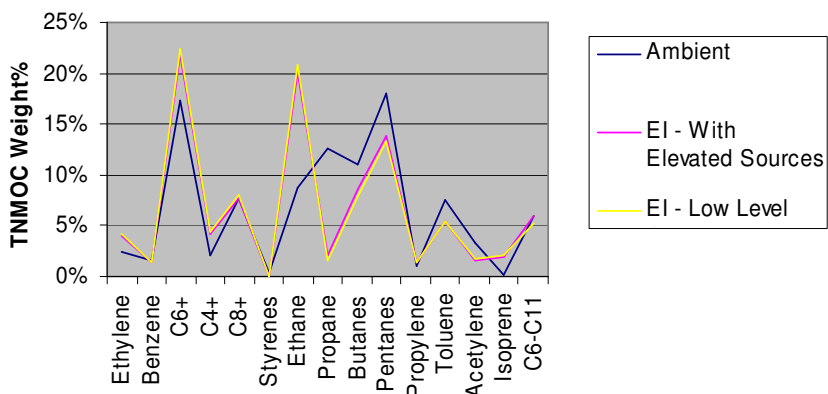


Figure 45. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Bakersfield Golden State site.

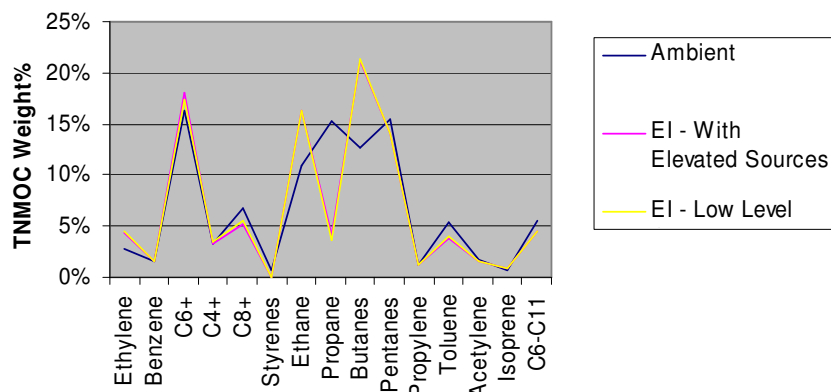


Figure 46. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Shafter site.

INTEGRATION OF PREVIOUS RESEARCH

In general, trends show that emission inventories have been moving toward closer agreement with ambient monitoring data over time. For example, **Figure 47** presents a series of comparisons between ambient- and emission inventory-derived VOC/NO_x ratios at the Los Angeles North Main monitoring site during summer mornings (Chinkin et al., 2005). This figure shows that ambient VOC/NO_x ratios have declined over time and that recent emission inventory-derived ratios agree much more closely with the ambient data than in past years.

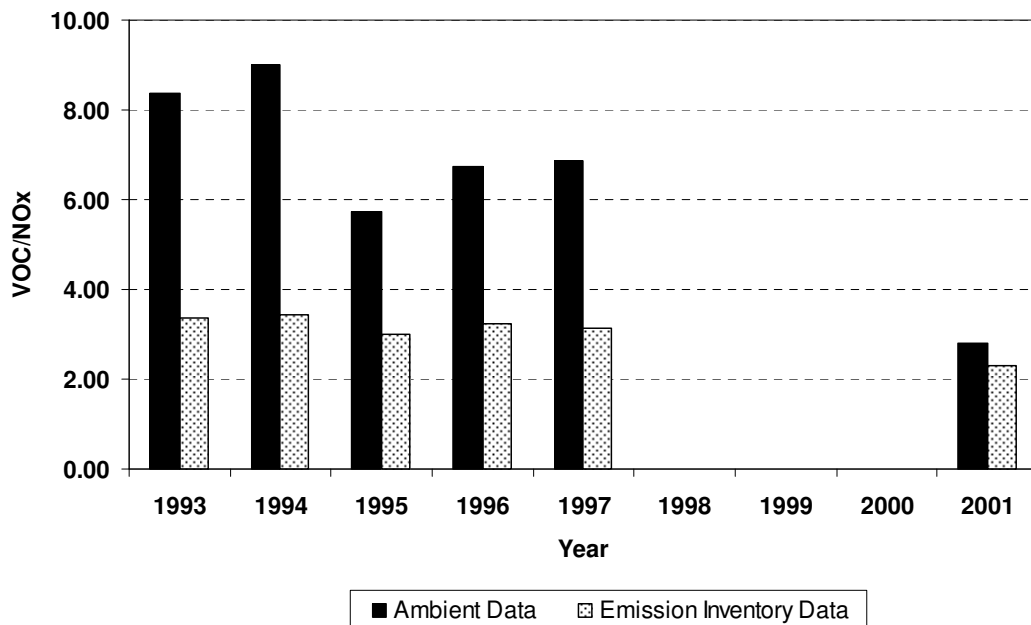


Figure 47. Ambient- and emission inventory-derived VOC/NO_x ratios at Los Angeles North Main during summer mornings.

A similar pattern can be seen in emissions reconciliation work that has been conducted in Central California, with emission inventory-derived pollutant ratios calculated for this project generally comparing more favorably with ambient-derived ratios than was the case with previous emission inventories. In a previous CCOS study performed by the Desert Research Institute (DRI) (Fujita et al., 2005), trends in the consistency between emission inventory estimates and ambient measurements were analyzed by calculating ambient- and emission inventory-derived TNMOC/NO_x ratios. While the techniques used in this study differ from those employed in the current project (i.e., basin-wide emission estimates were used instead of a spatially resolved modeling inventory), the overall trends do show an improvement in the agreement between emission inventory estimates and ambient data. **Table 6** shows the ratios of ambient- and emission inventory-derived TNMOC/NO_x ratios from the previous and current CCOS studies.

Table 6. Comparison of ambient- and emission inventory-derived TNMOC/NO_x ratios.

Air Basin	Ambient/Emission Inventory Ratio			
	DRI 1990	DRI 1995	DRI 2000	STI 2000 ^a
Sacramento	2.2	1.6	1.7	1.4 – 2.4
Fresno	3.6	2.6	1.9	1.4 – 7.2
Kern	—	3.9	2.9	2.6 – 4.3

^a This column shows the range of results from all sites evaluated in a given air basin, including both urban and rural sites.

Other studies compared emission inventory data to ambient data in central California:

- A comparison of ambient data collected during the Integrated Monitoring Study (IMS95) conducted during fall and winter of 1995-96 (Haste et al., 1998). This study compared ambient weekday data collected at sites in Fresno and Kern County from December 9, 1995, through January 6, 1995, to a gridded emissions inventory.
- A comparison of Photochemical Assessment Monitoring Stations (PAMS) monitoring data collected during the summer of 1996 with county-level emissions data from Fresno and Sacramento counties (Haste and Chinkin, 1999).
- A comparison of ambient data collected during the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) from December 18, 2000, through January 18, 2001, to a gridded emission inventory. Comparisons were made for sites in the Bay Area, Sacramento, Fresno, and Bakersfield.

Comparisons of results from the analysis of PAMS data in summer 1996 and in the current project are shown in **Figures 49 through 52**.

Figures 49 and 50 compare pollutant ratios for sites in the Sacramento area. Figure 49 shows that the ratio between ambient- and emission inventory-derived TNMOC/NO_x ratios for the Folsom site improved from 2 to 1.5 between the summers of 1996 and 2000. A slight improvement can also be seen in the ratio between ambient- and emission inventory-derived

TNMOC/NO_x ratios at the Del Paso Manor site over that same period (with the ratio decreasing from 2.3 to 2.1), and a significant improvement can also be seen in the CO/NO_x ratios at that site (see Figure 50).

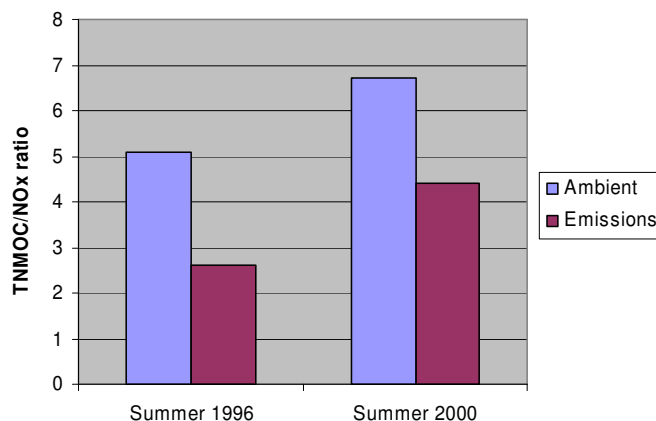


Figure 49. Trends in ambient- and emission inventory-derived TNMOC/NO_x ratios at the Folsom site.

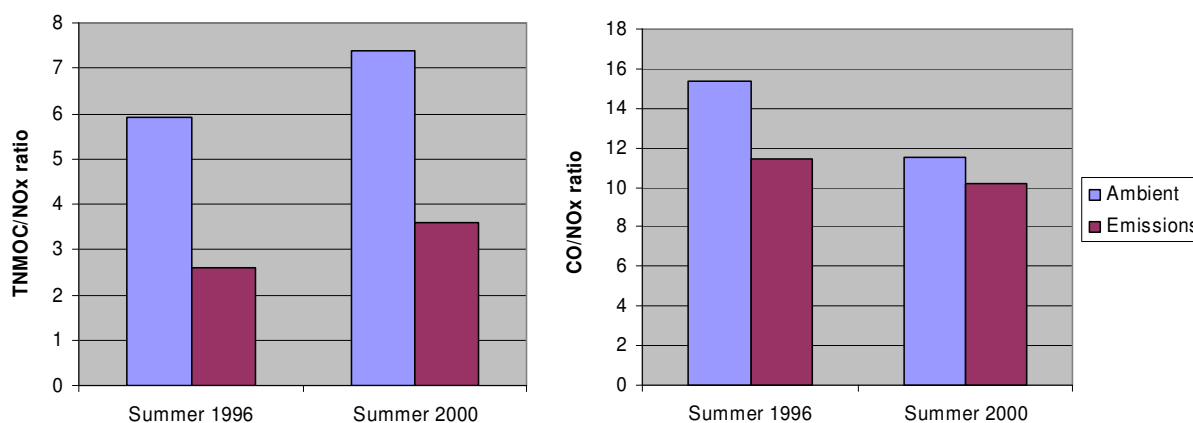


Figure 50. Trends in ambient- and emission inventory-derived TNMOC/NO_x (left plot) and CO/NO_x (right plot) ratios at the Sacramento Del Paso site.

Figures 51 and 52 compare pollutant ratios for sites in the Fresno area. Figure 51 shows that the ratio between ambient-and emission inventory-derived TNMOC/NO_x ratios for the Clovis site improved from 3 to 1.9 between the summers of 1996 and 2000, while the ratio of CO/NO_x ratios improved from 2.7 to 2.2. Improvement can also be seen at the Fresno First Street site, particularly for TNMOC/NO_x ratios (the ratios between ambient- and emission inventory-derived ratios improved from 2.7 in 1996 to 1.3 in the current study).

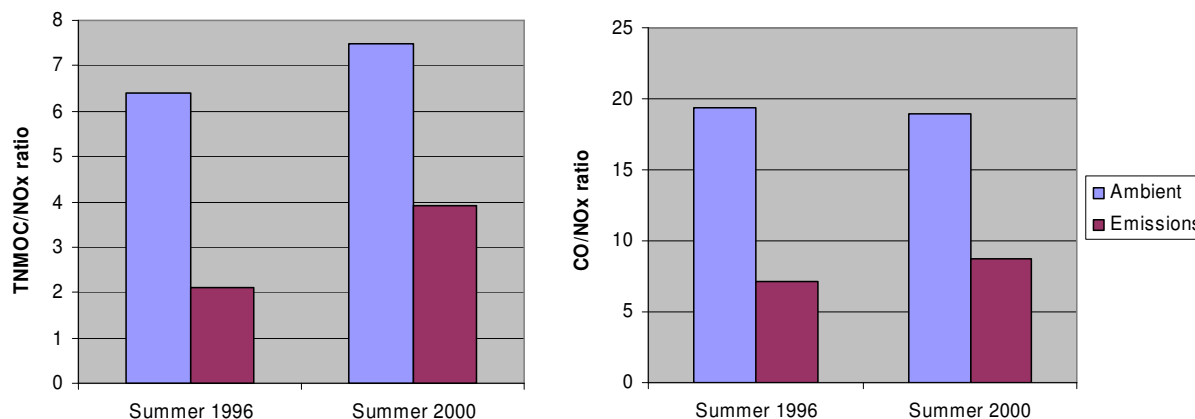


Figure 51. Trends in ambient- and emission inventory-derived TNMOC/NO_x (left plot) and CO/NO_x (right plot) ratios at the Clovis site.

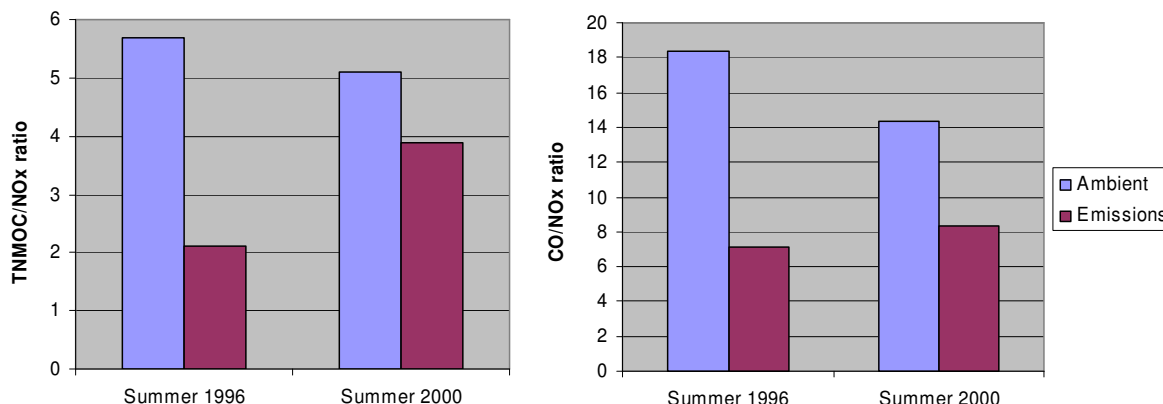


Figure 52. Trends in ambient- and emission inventory-derived TNMOC/NO_x (left plot) and CO/NO_x (right plot) ratios at the Fresno First Street site.

SUMMARY AND RECOMMENDATIONS

Overall findings for the CCOS emissions reconciliation are summarized below:

- When compared with other emissions reconciliation studies, the emission inventory data used in this project are generally in better agreement with ambient data than data in previous emission inventories.
- At some sites, the emission inventory data correlate with ambient data as closely as could be expected given the limitations of the comparison techniques used.
- For urbanized areas in the northern part of the CCOS modeling domain (the Sacramento area), the gridded emission inventory data are in good agreement with data from ambient monitoring sites on weekdays, but show poorer agreement on weekend days.

- For urbanized areas in the central part of the CCOS modeling domain (the Fresno area), the gridded emission inventory data are in good agreement with data from ambient monitoring sites on both weekdays and weekend days.
- For urbanized areas in the southern part of the CCOS modeling domain (Bakersfield), the gridded emission inventory data do not show good agreement with ambient monitoring data on either weekdays or weekend days.
- For most rural areas in the CCOS modeling domain, the gridded emission inventory data do not show good agreement with ambient monitoring data on either weekdays or weekend days. However, these sites do not fully meet the underlying assumptions of the analysis techniques used (i.e., significant local emissions around the monitoring site).

Based on the findings from this study, STI recommends that the following steps be taken to further investigate the CCOS modeling emission inventories and to make specific improvements to those inventories:

- Improve the accuracy of weekend emission estimates in the Sacramento area. Because monitoring sites in Sacramento are likely to be primarily influenced by on-road mobile source emissions, weekend vehicle activity data should be collected and used to better characterize differences in weekday and weekend day travel.
- A correction should be made to the spatial distribution of emissions from livestock waste in the existing emission inventory. (This update should resolve the discrepancies between the ethane fractions observed in the ambient and emission inventory data).
- Further investigate the poor agreement between ambient and emission inventory data in Kern County. Given that the comparison between ambient and emission inventory data is generally good at urban sites dominated by mobile sources, it may be that other source types are poorly characterized in Kern County. Source apportionment techniques, such as PMF⁸ or bottom-up efforts to “ground truth” the Kern County inventory could be used to identify specific areas of improvement.
- Collect more ambient data at Bay Area sites. The possible comparisons between ambient and emission inventory data were very limited in this project given the availability of data from Bay Area sites.

⁸ Limited PMF analyses are scheduled to be done as part of the current study with assistance from the Bay Area Air Quality Management District. No source apportionment results were ready at the time this document was prepared.

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APPENDIX D

WILDFIRE EMISSIONS REVIEW FINDINGS AND RECOMMENDATIONS FEBRUARY 22, 2007



Sonoma Technology, Inc.

TECHNICAL MEMORANDUM

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February 22, 2007

STI-905044.10-3145-TM

TO: Dr. Patricia Velasco, California Air Resources Board

FROM: Lyle R. Chinkin, President
Sean M. Raffuse, Senior Air Quality Analyst, GIS Services Group
Stephen B. Reid, Manager, Emissions Assessment Group

RE: Wildfire Emissions Review Findings and Recommendations – Comparison of Ambient Measurements to Emissions Representations for Modeling

This technical memorandum is a deliverable for the “Central California Ozone Study (CCOS) – Comparison of Ambient Measurements to Emissions Representations for Modeling” project. The CCOS is a multi-year program of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. The CCOS was initiated for the purpose of improving the scientific understanding of ozone air quality problems in northern and central California. The goals of CCOS are being met through analysis of existing data; a large-scale field study conducted in summer 2000 to acquire a comprehensive database to support modeling and data analysis; analysis of the data collected during the field study; and the development, evaluation, and application of an air quality simulation model for northern and central California. This CCOS project complements other CCOS activities. Sonoma Technology, Inc. (STI) investigated why preliminary CCOS photochemical modeling results differ from ambient observations by comparing emissions and ambient data.

The purpose of this technical memorandum is to provide the CCOS Technical Committee (TC) with an assessment of the wildfire emission estimates used for CCOS photochemical modeling efforts and to recommend improvements for the characterization of wildfire emissions.

BACKGROUND

Two large wildfires occurred in the CCOS modeling domain during the July 29–August 3, 2000, ozone episode. The Manter fire burned a 73,000-acre area in Tulare County from July 22–August 8, 2000, and the Plaskett fire burned a 58,000-acre area in Monterey County from July 23–31, 2000. Due to the timing and scale of these fires, ARB staff decided to estimate daily emissions from them in order to assess their potential impact on regional photochemistry (Scott, 2003).

Wildfire emission estimates were prepared by U.C. Berkeley's Center for the Assessment and Monitoring of Forest and Environmental Resources (CAMFER) laboratory using its Emissions Estimation System (EES) model. In brief, daily emission estimates were produced by the EES model using

- daily fire perimeters derived from geopositioning satellite (GPS) data collected during helicopter overflights;
- fuel (biomass) types derived from U.C. Santa Barbara's Gap Analysis Program (GAP) vegetation data, a geographic information systems (GIS)-based data layer;
- emission algorithms, combustion efficiencies, fuel loadings, and other parameters from the First Order Fire Effects Model (FOFEM); and
- a fuel moisture estimate taken from a U.S. Department of Agriculture Forest Service (USFS) Wildland Fire Assessment System (WFAS) map image for July 22.

EES generates daily emission estimates for both the flaming and smoldering¹ phases of fires, though emissions from the two phases are combined in final model outputs. Daily emissions are allocated to hours of the day using a temporal profile from a report published by the Fire Emissions Joint Forum (FEFJ) of the Western Regional Air Partnership (WRAP) (Air Sciences, 2004).

The vertical distribution of wildfire emissions was modeled using an approach described in the same WRAP report. Acreage and fuel loading data for each fire event were used to classify fires into size classes based on "virtual acreage". The size classes were then used to determine the fire's buoyancy efficiency, plume bottom height, plume top height, and the fraction of emissions fumigated into the first model layer. The fraction of emissions assigned to the plume (rather than the first model layer) was distributed evenly over release points at heights of 25 m, 75 m, and 100 m, then at every 100 m up to the plume top height.

¹ The smoldering phase of a fire is characterized by a lower combustion efficiency than that of the flaming phase, which results in increased levels of smoke production. Emissions of volatile organic compounds (VOC) are primarily associated with the smoldering phase, while emissions of nitrogen oxides (NO_x) are primarily associated with the flaming phase.

ANALYSIS

ARB provided STI with air quality model-ready (i.e., gridded, hourly, vertically distributed) point source emission files that included wildfire emissions. STI analyzed the spatial and temporal characteristics of the wildfire emission estimates and evaluated alternative methods and data sets that could be used to improve the characterization of model-ready wildfire emissions.

The temporal distribution of emissions of total organic gas (TOG) and nitrogen oxides (NO_x) from the Manter fire during the July/August 2000 episode is shown in **Figure 1**. This figure shows that, while the magnitude of TOG emissions is approximately 3 times higher than the magnitude of NO_x emissions, the temporal distribution of both pollutants is identical.

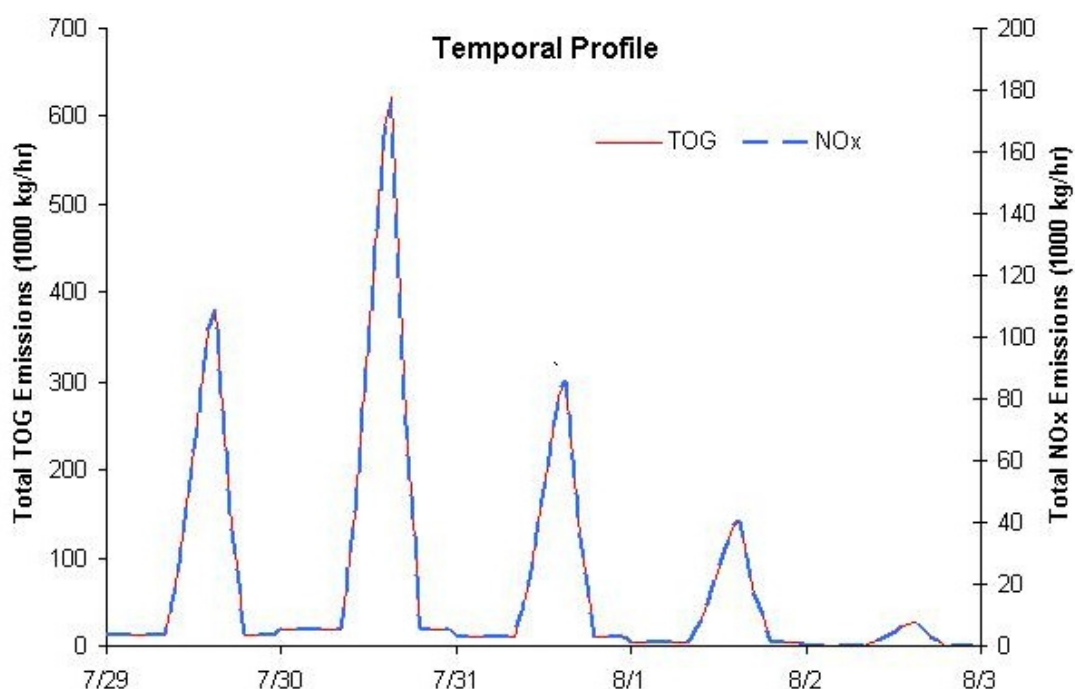


Figure 1. Temporal distribution of wildfire emissions for the Manter fire.

Similarly, the spatial allocation of TOG and NO_x emissions from the Manter fire to individual grid cells in the modeling domain is shown in **Figure 2**. This figure shows that, while spatial patterns of emissions vary from day to day as the fire perimeter changes, the spatial distribution of TOG and NO_x emissions are identical.

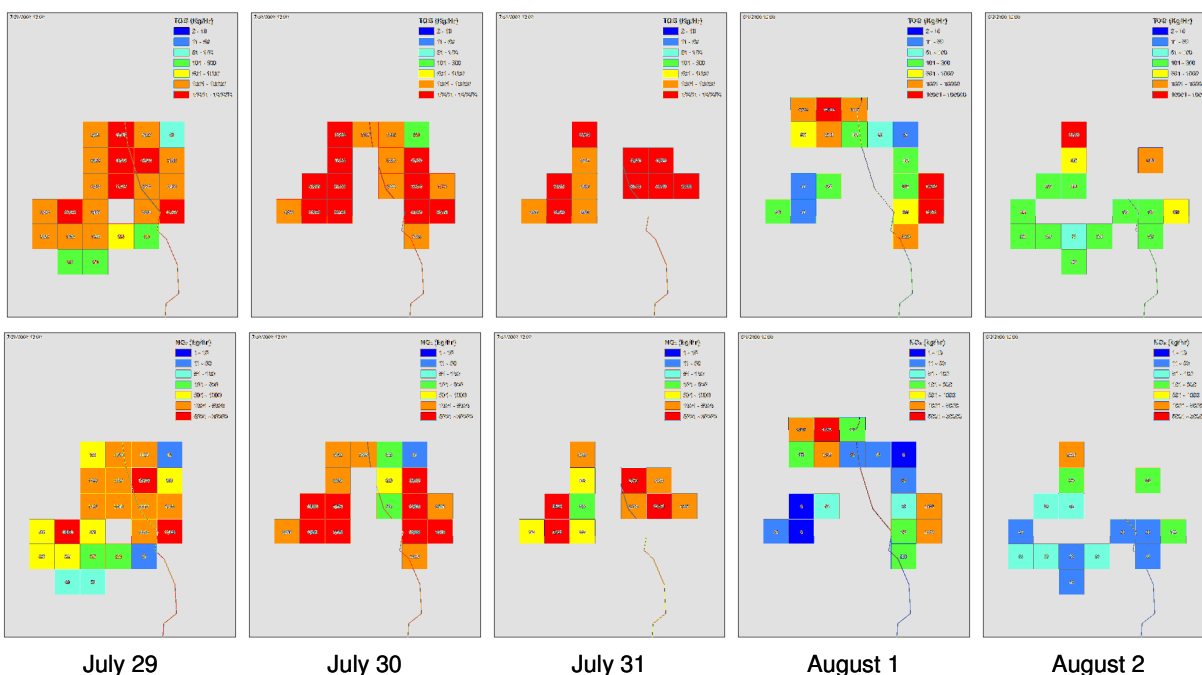


Figure 2. Spatial distribution of wildfire TOG (top row) and NO_x (bottom row) emissions for the Manter fire.

The vertical distribution of wildfire emissions was achieved by treating the emissions associated with various grid cells and hours as discrete “point sources” with varying pseudo-stack heights. These stack heights were estimated based on the WRAP methodology described above, which calculates a fraction of emissions fumigated into the first layer, then evenly distributes the remaining emissions from an estimated plume bottom height to an estimated plume top height. **Table 1** shows the default pseudo-stack parameters assigned to wildfire emissions in the CCOS model-ready point source files, and one can see that the stack heights range from about 3 to 2,000 meters.

Table 1. CCOS wildfire stack parameters.

Stack parameter	Value
Height	3 m - 1,923 m (varies by hour)
Diameter	0.3 m
Exit temperature	72°F
Exit velocity	4 m/s

The resulting vertical structure of TOG and NO_x emissions from the Manter fire is shown in **Figure 3**. This figure shows that the plume bottom/top method used to allocate emissions vertically results in a gap between the plume bottom and the lowest model layers. In addition,

while the overall vertical distribution of emissions varies from hour to hour, the vertical distribution of TOG and NO_x emissions is identical for each hour.

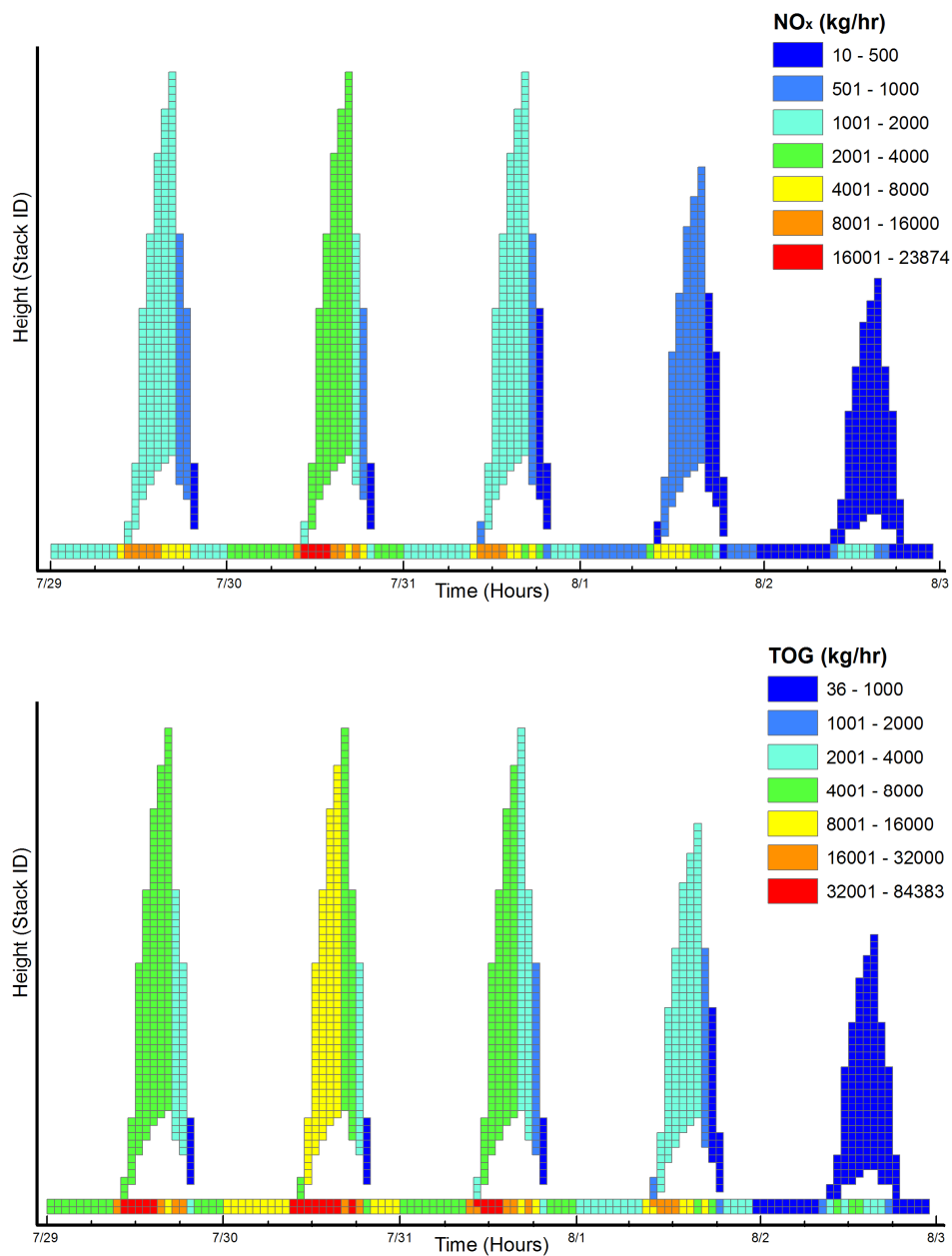


Figure 3. Vertical distribution of wildfire emissions for the Manter fire. Height bins are at 25 m, 75 m, and 100 m, then at every 100 m up to the plume top height.

FINDINGS

In general, emissions from the Manter and Plaskett fires were reasonably estimated on a daily scale, given the available data. However, issues exist with the temporal, spatial, and vertical distribution of emissions. In particular, the combination of flaming and smoldering emissions resulted in allocating emissions from these phases identically in time and space, even though the two phases are likely to have very different temporal and spatial characteristics. Smoldering combustion is lower in intensity than flaming combustion, which results in the smoldering phase lasting longer and resulting in less lofted smoke than occurs in the flaming phase. Also, the lower intensity of smoldering emissions results in the production of more particulate matter (PM) and TOG emissions and fewer NO_x emissions relative to flaming.

One practical consequence of the differences between the smoldering and flaming phases is that the current hourly allocation of wildfire emissions in the CCOS modeling inventories may not adequately take into account the duration of smoldering emissions. The U.S. Environment Protection Agency (EPA) has developed state-specific temporal profiles for wildfire emissions using the USFS' Emission Production Model (EPM), which estimates hourly emissions from individual fires and from subsequent smoldering. Hourly profiles developed for individual states reflect the relative composition of biomass fuels found in each state (Batty, 2004). **Figure 4** shows the comparison of the EPA diurnal profile for wildfires in California with the diurnal profile used in the CCOS modeling; and while both profiles show a peak in emissions during the late afternoon, the EPA profile distributes a greater proportion of emissions to the night and morning hours.

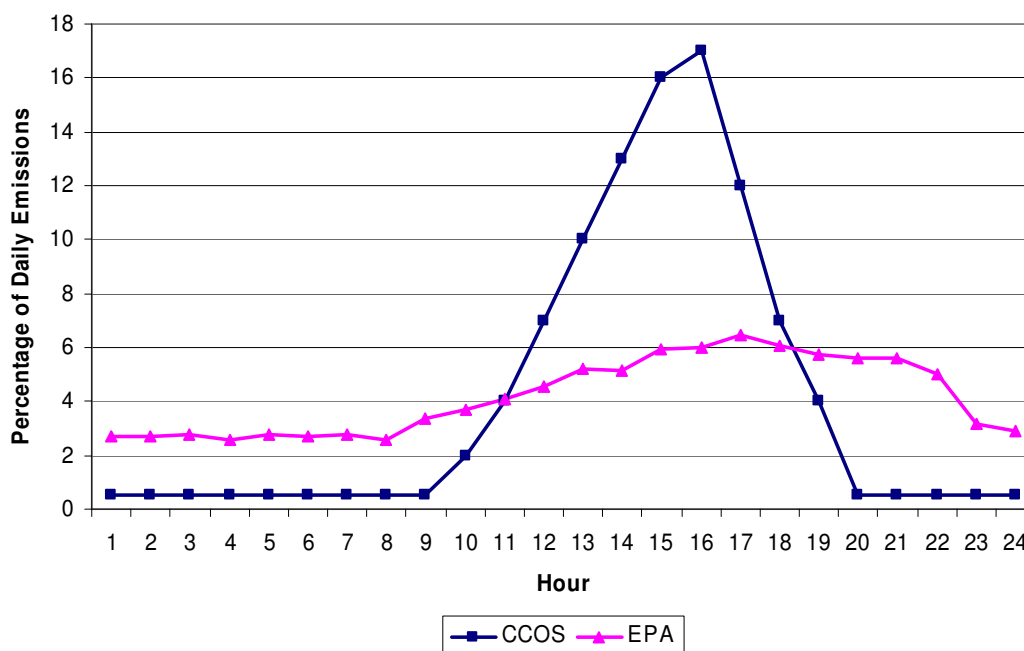


Figure 4. Diurnal profiles for wildfire emissions.

Also, because of the longer duration associated with the smoldering phase, USFS representatives have recommended that emission estimates from FOFEM and other fuel consumption models be adjusted to account for additional smoldering emissions occurring in the days following a fire (Boyer et al., 2004). During the development of the 2002 WRAP fire emission inventory, once emissions were estimated for a given fire, additional smoldering emissions were assigned to the same burn location on the following calendar day if “heavy” fuels were being burned (Air Sciences, 2004). Accounting for ongoing smoldering emissions in this way would change the relative spatial distribution of TOG and NO_x emissions for a multi-day burn, as TOG-rich smoldering emissions from the previous day’s burn “footprint” would be incorporated into emission estimates for subsequent days.

Finally, another important consideration is the treatment of wildfire emission estimates within the air quality model. CCOS photochemical modeling has been performed with the Comprehensive Air Quality Model with extensions (CAMx), a model that calculates the internal plume rise for point sources.² This plume rise calculation is made based on stack parameters (height, diameter, exit temperature, and exit velocity) and meteorological conditions (ambient temperature and wind speed). Because the pseudo-stack height is already being used to set the vertical level of wildfire emissions for a given hour and grid cell, the remaining pseudo-stack parameters should result in no additional plume rise being assigned to these emissions within the air quality model. However, analysis of CAMx outputs obtained in a related CCOS project being carried out by STI has shown that, in some cases, the default pseudo-stack parameters assigned to wildfire emissions in the CCOS model-ready point source files (see Table 1) result in the calculation of a significant plume rise within CAMx.³ **Figure 5** displays a three-dimensional representation of “tracer” emissions from the Manter fire derived from CAMx outputs, and this figure shows that emissions intended to rise no higher than 2 km are actually rising to well over 10 km.

² Other photochemical grid models, such as the Community Multiscale Air Quality model (CMAQ), require that emissions be vertically resolved prior to being input into the air quality model.

³ The plume rise calculation is based, in part, on the difference between the stack temperature and the ambient temperature. In elevated parts of the Sierra Nevada Range, the ambient temperatures at certain hours are well below the 72°F stack temperature used as a default for wildfires.

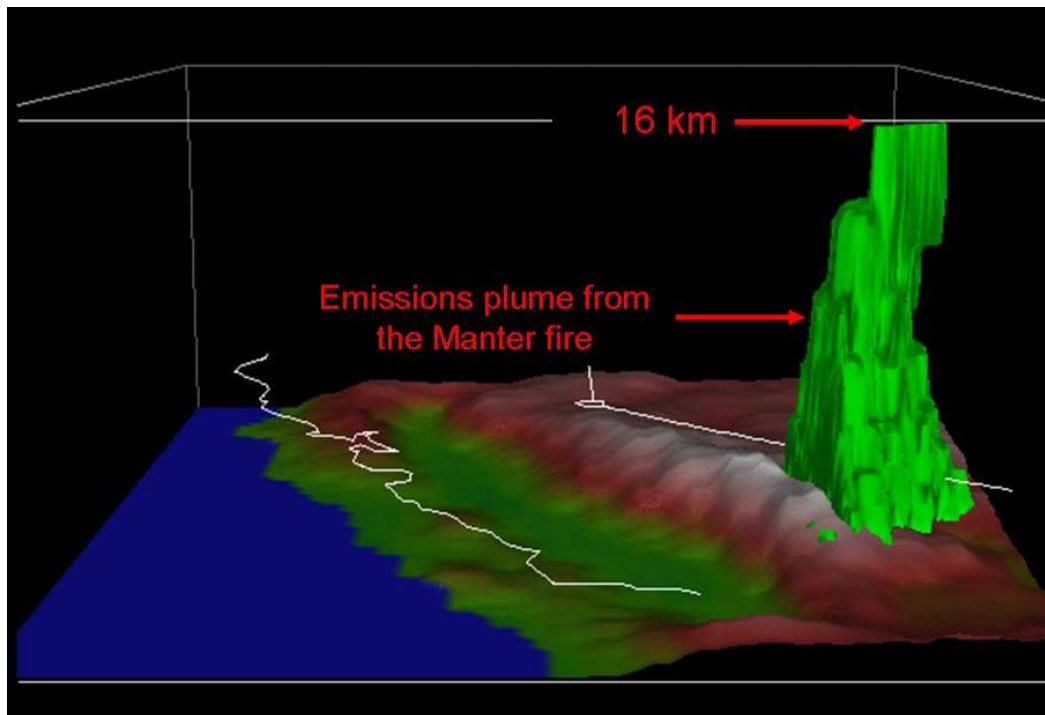


Figure 5. Vertical distribution CAMx tracer emissions from the Manter fire for July 29, 2000 at 7:00 PM PDT.

RECOMMENDATIONS

Based on the findings outlined above, STI makes the following recommendations for improving the characterization of wildfire emissions and for conducting further investigations:

- Pseudo-stack parameters assigned to wildfires should be set to levels that ensure that no plume rise is calculated within CAMx.⁴
- EES model outputs should be adjusted to account for ongoing “second day” smoldering emissions (this step would also alter the spatial distribution of emissions).
- Because of the differences in characteristics between smoldering and flaming emissions, we advise the use of different diurnal distributions for TOG and NO_x emissions from wildfires. In the absence of better data, the EPA temporal profile shown in Figure 4 should be used in place of the current temporal profile to represent the diurnal distribution of TOG emissions. This EPA profile takes into account “second day” smoldering emissions and may be more representative of total hourly TOG emissions than the current temporal profile.

⁴ Alternatively, in CAMx, it is possible to disable the internal plume rise calculation (ENVIRON International Corporation, 2006).

As part of a related CCOS project, STI is currently performing CAMx sensitivity runs to investigate the impact of the current plume rise scheme. It is recommended that the impact of each of the potential improvements listed above be similarly tested before adoption.

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APPENDIX E

PHASE II SOURCE APPORTIONMENT FINDINGS

October 31, 2008

STI-905044.14-3396-TM

To: Cheryl Taylor, California Air Resources Board, Planning and Technical Support Division

From: Steve Brown, Tami Funk, Jessie Charrier, Erin Gilliland, Hilary Hafner, and Steve Reid

Re: Phase II source apportionment findings (extension to the CCOS project “Comparison of Ambient Measurements to Emissions Representations for Modeling”)

SUMMARY

At the direction of the Central California Ozone Study (CCOS) Technical Committee (TC), Sonoma Technology, Inc. (STI) conducted source apportionment analyses using ambient air quality data from monitoring sites in the CCOS domain. During a preliminary data evaluation, STI grouped these sites into three tiers: Tier 1 sites have data characteristics most likely to support meaningful source apportionment analyses; data from Tier 2 sites are somewhat likely to support such analyses; and data from Tier 3 sites are least likely to support such analyses. However, data from Tier 1 sites, while most suitable for further analysis among the selected sites, were not ideal because the number of samples and the precision of the data remain low. Results of source apportionment analyses of Tier 1 sites enabled the identification of approximate contributions from major sources, and these results can be useful to direct further efforts in assessing the emissions inventory. A summary of results by site and analysis is shown in **Figure 1**.

Among the three Tier 1 sites—Bakersfield Golden State (BGS), Clovis (CLO), and Sacramento Del Paso Manor (SDP)—ambient total nonmethane organic compounds (TNMOC) concentrations were highest at the Bakersfield site, exceeding TNMOC concentrations at the Sacramento and Clovis sites by about 75% and 45%, respectively (see Figure 1). However, the TNMOC emission inventory (EI)¹ for the grid analysis zone² around each monitoring site shows that TNMOC emissions are lowest at the Bakersfield site and highest at the Sacramento site (see **Figure 2**). That the EI reconciliation work showed relatively good agreement between the EI and ambient data at the Sacramento site (Chinkin and Reid, 2006) indicates the overall TNMOC inventory is likely to be underpredicted at both the Clovis and Bakersfield sites.

¹ To make consistent comparisons of TNMOC between the ambient data and emission inventory, only the species measured at the monitoring sites were included in the emission inventory summaries.

² The grid analysis zone around each monitoring site was determined during the EI reconciliation work based on predominant wind speeds (Chinkin and Reid, 2006) .

At the Sacramento site, positive matrix factorization (PMF) and chemical mass balance (CMB) provided similar results overall when examining the 0500 PDT year-2000 ambient volatile organic compound (VOC) data. The majority of TNMOC was determined to be contributed by mobile sources or was unidentified by the chemical analysis (the relative amount of unidentified mass is highest in Sacramento compared with Clovis and Bakersfield). When the breakdown of identified TNMOC from the source apportionment analyses was plotted against results from the EI, the mobile source contribution in the EI (61%) fell within the range of mobile source TNMOC contributions from the PMF (50%) and CMB analyses (66%), as shown in **Figure 3**. The contribution of biogenic emissions to TNMOC was higher in the EI than in the source apportionment analyses, which may be due to the fact that biogenic emissions are highly reactive and often present in concentrations that are below the detection limit of ambient monitoring equipment. Alternatively, this finding may result from a bias in the biogenic emissions model used to develop these emission estimates. Overall, these results corroborate the findings from the EI reconciliation work, which indicated that the EI and ambient data showed relatively good agreement at the Sacramento site.

Clovis had a mediocre agreement between the EI and ambient data. The EI has almost 60% of the TNMOC emissions in the region due to stationary sources (see **Figure 4**), while the CMB/PMF results suggested that over 60% of the identified TNMOC mass is mobile in origin. An adjustment of the EI to reflect more mobile source influence would likely result in better agreement between the EI and ambient data at Clovis.

At Bakersfield, the EI compared poorly with the ambient data, with ambient-derived TNMOC/NO_x ratios being three to four times higher than emission inventory-derived ratios (Chinkin and Reid, 2006). The EI shows less than half of the TNMOC attributed to mobile sources, while the CMB/PMF results suggest mobile sources account for 55% to 61% of the identified TNMOC mass (see **Figure 5**). These results suggest that mobile sources are under-represented in the EI around the Bakersfield site, though stationary source emissions are likely to be under-estimated as well, given the relatively low TNMOC emissions associated with this site.

Overall, these results indicate that TNMOC emissions are under-estimated at Bakersfield (and possibly Clovis), and that mobile sources are under-represented in the EI at Clovis and Bakersfield. The ambient data used in source apportionment analyses is limited in terms of number of samples and precision, as discussed in earlier work. While there is a high amount of confidence in the results overall, there is less confidence in more detailed trends or breakdowns among source types. These details, as well as multiple year trends, could be further explored by conducting a similar analysis on data from 2001-2004. These data are more abundant and have better precision, increasing the confidence in results. For example, with an increased number of samples and analytical precision, additional sources could be resolved or current sources better resolved.

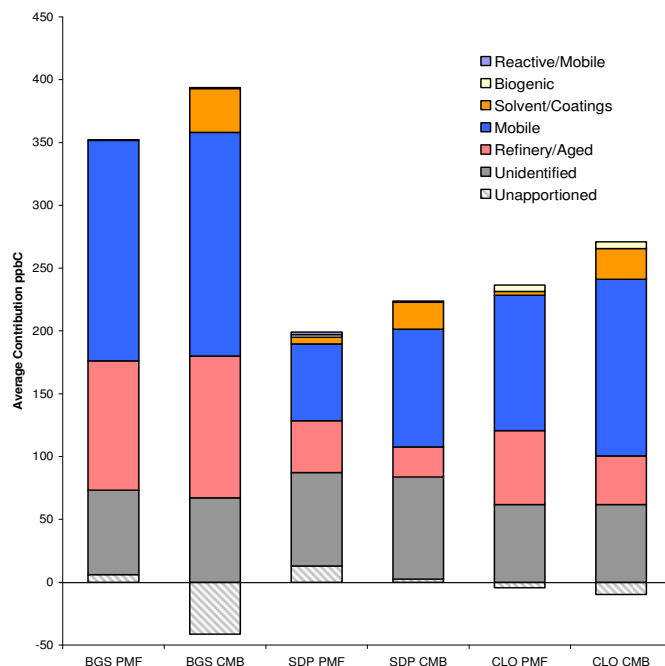


Figure 1. Summary of CMB and PMF analyses by site for 3-hr summer VOC samples at 0500 PDT in 2000. PMF analyses were conducted using 1996-2000 data to provide a large enough data set to perform reasonable analyses; only the 0500 PDT samples in 2000 are shown. Mass that could not be accounted for by the source apportionment model is unapportioned; a negative value indicates over-apportionment.³ Unidentified mass is the difference between TNMOC and the sum of Photochemical Assessment Monitoring Stations (PAMS) target compounds; this mass was not included in the source apportionment models.

³ In CMB analyses, the unapportioned mass (mass not accounted for by available source profiles) can be positive (under-apportionment) or negative (over-apportionment). The typical range of acceptable CMB mass apportionment is $100 \pm 20\%$ (Coulter, 2004).

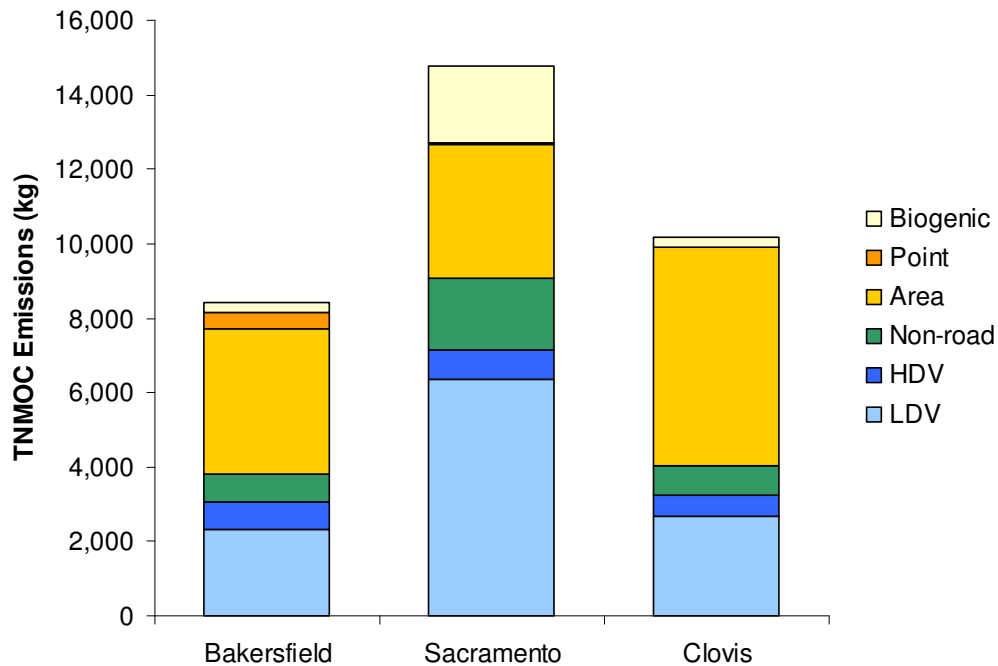


Figure 2. Summary of 0500 to 1000 PDT TNMOC emissions from the EI by source category.

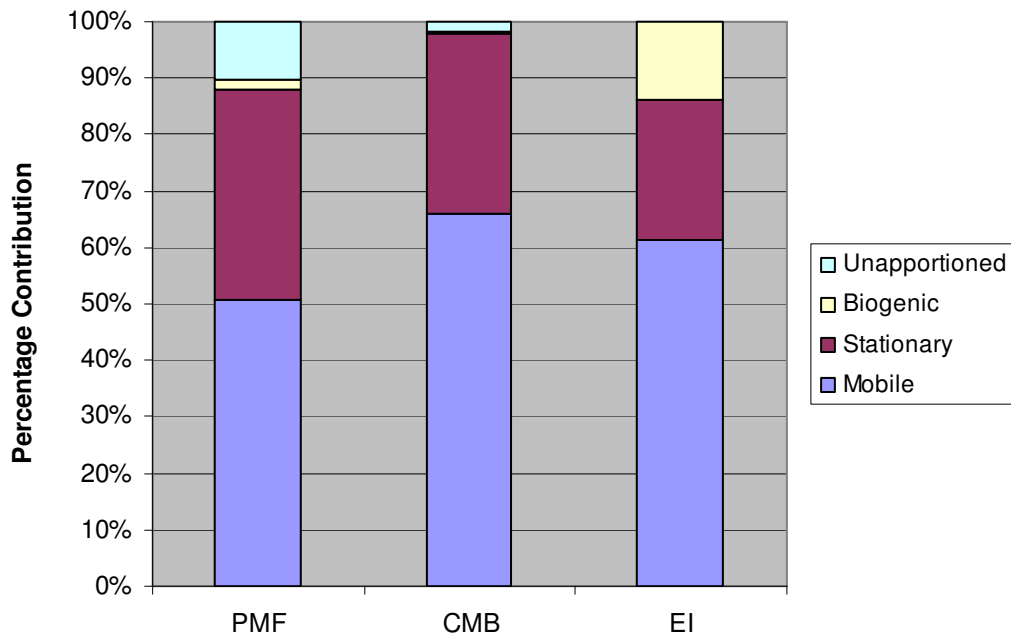


Figure 3. Comparison of source contributions to 0500 to 1000 PDT TNMOC at the SDP site from source apportionment analyses and the EI.

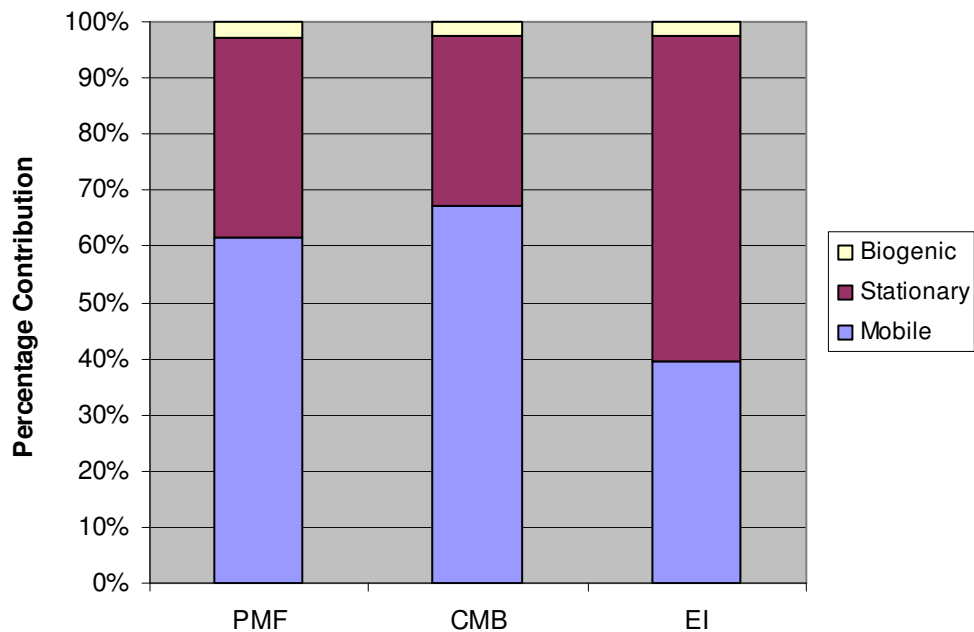


Figure 4. Comparison of source contributions to 0500 to 1000 PDT TNMOC at the CLO site from source apportionment analyses and the EI.

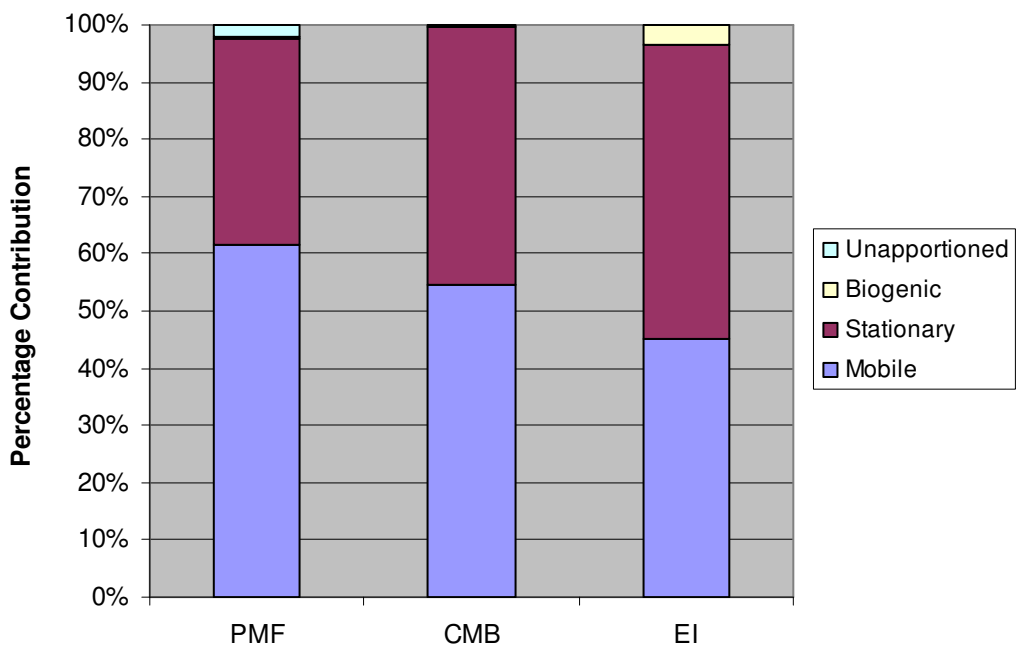


Figure 5. Comparison of source contributions to 0500 to 1000 PDT TNMOC at the BGS site from source apportionment analyses and the EI.

INTRODUCTION

Receptor modeling is the process of applying multivariate statistical methods to help identify and quantify air pollutants and their corresponding emissions sources. The chemical mass balance (CMB) and positive matrix factorization (PMF) models are two of several receptor models that have been applied to better understand observed pollutant compositions and emissions source influences. Receptor models use the chemical and physical characteristics of gases and particles from a particular emissions source and receptor to identify the presence of and to quantify source contributions to receptor concentrations (http://www.epa.gov/scram001/receptor_cmb.htm).

This memorandum describes the CMB and PMF analyses performed on ambient data collected during Central California Ozone Study (CCOS) (summer 1996-2000) to (1) determine relative emissions source contributions to total VOC mass observed in the ambient air, and (2) to assess how well the source contributions, identified using receptor models, compare to TNMOC emission breakdowns by source category in the emission inventory (EI). The results of the CMB and PMF analyses can then be compared to the EI to identify important emissions source types and to recommend improvements to the application of speciation profiles used for EI development.

BACKGROUND

At the direction of the CCOS Technical Committee (TC), Sonoma Technology, Inc. (STI) evaluated the suitability of ambient air quality data from monitoring sites in the CCOS domain for source apportionment analyses. During a preliminary data evaluation, STI grouped these sites into three tiers: Tier 1 sites have data characteristics most likely to support meaningful source apportionment analyses; data from Tier 2 sites are somewhat likely to support such analyses, and data from Tier 3 sites are least likely to support such analyses.

This work is an extension of the “Comparison of Ambient Measurements to Emissions Representations for Modeling” project, which is sponsored by the San Joaquin Valley Air Pollution Study Agency (SJVAPSA) in support of the CCOS. During this project, STI investigated why preliminary CCOS photochemical modeling results differ from ambient observations by comparing emissions and ambient data. Several techniques were used to make comparisons between CCOS EI estimates and ambient data, including a review of the total organic gas (TOG) speciation profiles used by the California Air Resources Board (ARB) to prepare emission inventories for air quality model runs and a reconciliation of emissions data and ambient data by comparing emissions inventory- and ambient-derived pollutant ratios.

SCOPE OF WORK

The tasks included in this work were to conduct PMF and CMB analysis on ambient speciated VOC data at Sacramento Del Paso, Clovis, and Bakersfield monitoring sites collected during 1998-2000. CMB analysis focused on data collected in 2000 only; PMF analysis used the

1998-2000 data. These results were compared between the two methods, and summarized for comparison to the EI evaluation conducted previously.

Results from this task are intended to help the CCOS TC understand differences between source allocations from source apportionment in the ambient data and source distributions found in the EI data.

TECHNICAL APPROACH AND FINDINGS

Three PAMS sites in California were selected for source apportionment: Sacramento Del Paso, Clovis, and Bakersfield. **Figures 6 through 8** show Google Earth™ images of each site. PMF and CMB receptor modeling were applied to the ambient 3-hr data to better understand the source contribution at each site and ramifications for EI reconciliation. This dual-model approach was used to reduce the inherent limitations of both PMF and CMB in order to obtain more reliable results and to gain a better understanding of the source profiles, and their effectiveness in representing the ambient data. CMB requires that ambient data fit source profiles, which are representative of single source emissions and may not accurately reflect how emissions are transformed between source and receptor. PMF uses the natural variance in the ambient data to reduce the data to a set of factors, which are due to either a common source or meteorological phenomenon.

These analyses would result in a better understanding of

- the sources of VOC ozone precursors
- how well the source profiles account for the ambient VOC mass
- our relative confidence in the source profiles
- the degree of secondary formation and air mass age of the VOC samples
- the representativeness of the sites

We will include recommendations that can be directly used in photochemical modeling and in the reconciliation of the EI tasks.



Figure 6. Google Earth™ image of the Bakersfield monitoring location.

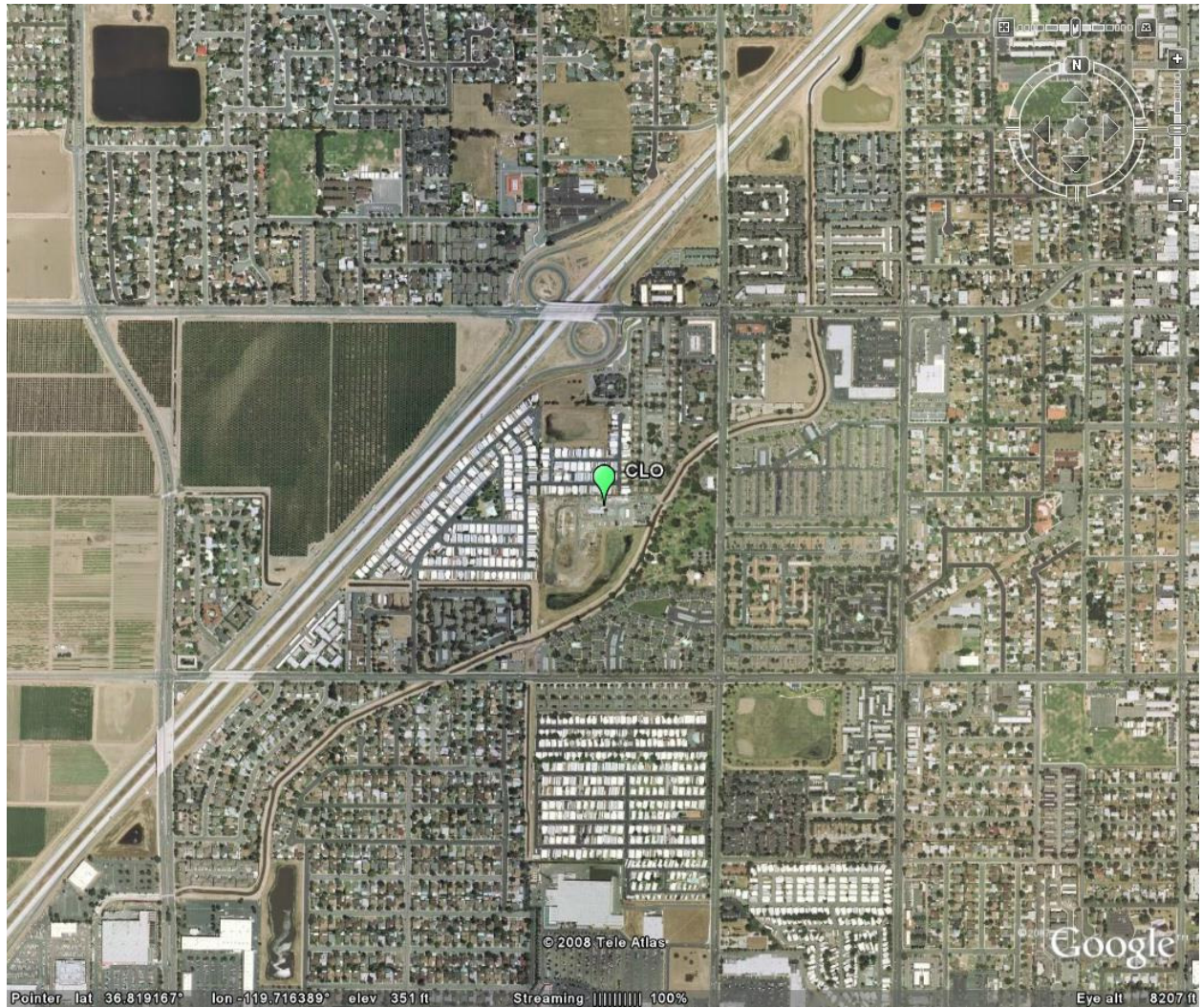


Figure 7. Google Earth™ image of the Clovis monitoring location.

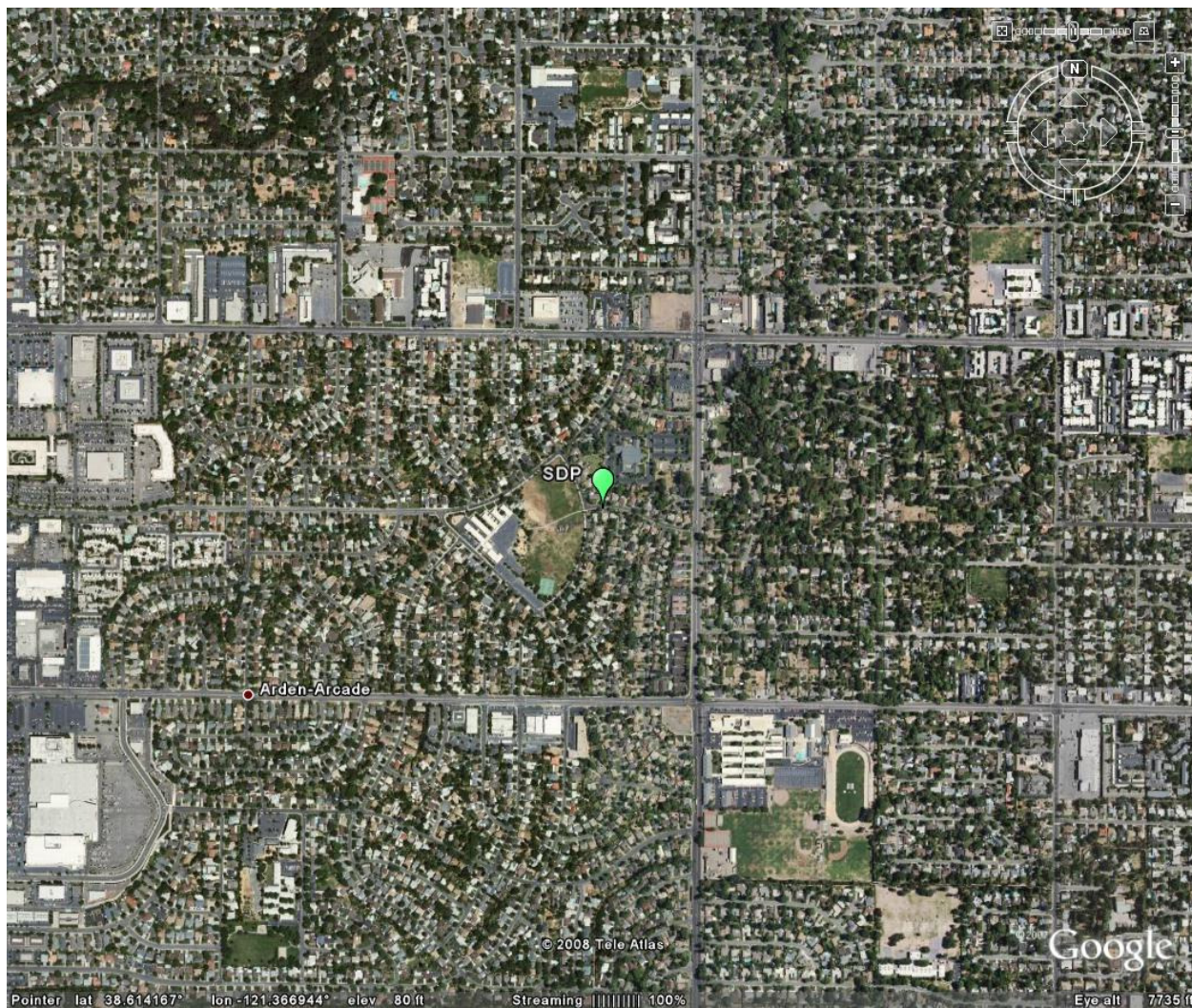


Figure 8. Google Earth™ image of the Sacramento Del Paso monitoring location.

Data Availability and Resolution

EI reconciliation was performed on 0500 PDT PAMS VOC measurements collected during summer 2000, making this the target data for comparison. However, this data set consists of less than 30 records for a given site. Thirty records are sufficient for CMB analysis, which performs source apportionment on one sample at a time, but is insufficient for PMF analyses. Additional years of data were included in the PMF analyses to increase the stability and statistical robustness of the results. This data set consisted of 1996-2000 all-hours data. The all-hours data included 3-hr samples taken at 0500 PDT, 1200 PDT, 1600 PDT, and 2300 PDT, except in 2000 when only 0500 PDT data was measured. The 1996-2000 time period was selected because it is the largest time period comparable to 2000, avoiding reformulated gasoline (RFG) changes that occurred in California in 1995 and base line changes apparent in data collected after 2000 due to new sampling methodology. Ratio analyses were performed at all sites to ensure that major source impacts had not changed over the 1996-2000 time period. As outlined in **Table 1**, the number of records available using 0500 PDT data for 2000 only was not

sufficient to obtain robust results. Therefore, the 1996-2000 all hours data set was used in PMF analyses. This had a mild impact on the PMF analyses because samples for which the air is more aged were included, but the results were not significantly altered. For comparison purposes, only the 0500 PDT samples in 2000 from the PMF analysis will be compared to the CMB results.

Table 1. The number of records available for two data sets used in CMB and PMF.

Site Abbreviation	Number of records available for 2000 0500 PDT data (CMB)	Number of records available for 1996–2000 all hours data (PMF)
Sacramento	20	519
Clovis	22	485
Bakersfield	26	508

While the larger data set assisted in the stability of PMF results, a loss of precision occurred for 2000 data that had been truncated or rounded to integers. This loss of resolution was especially detrimental to pollutants that exist at low ambient concentrations, and impacted both the CMB and PMF analyses.

Chemical Mass Balance (CMB) Analysis

CMB is a source apportionment method that solves a series of linear equations using a weighted least squares solution where each equation represents the concentration of a chemical species measured at the receptor as the sum of the products of source contributions and source profiles weighted by the user-supplied uncertainties (Watson, 1979). For each species i , the concentration of i measured at the monitoring site is the sum of source contributions from source j (S_j) times the fraction of S_j composed of species i (F_{ij}) for the number of sources (n) sources (Equation 1).

$$C_i = \sum_1^n F_{ij} S_j \quad (1)$$

The required inputs for running CMB are an ambient data set and source profiles along with associated uncertainties. The ambient data set includes concentrations measured at a monitoring site for each chemical species over time. Source profiles include the fractional contributions for each chemical species emitted by a source. Because source profiles are a required input, sources must be identified and their emissions characterized prior to running the CMB model, and it is important to use source profiles that are representative of local sources.

The CMB model has some inherent assumptions and limitations (Coulter, 2004; Watson, 2004). The model assumes that

- source emissions are constant,
- species do not react (i.e., conservation of mass),
- all sources at the receptor site have been identified with accurate source profiles, and
- there is no collinearity in the source profiles.

While these assumptions are not physically accurate in the ambient environment, the effect of these assumptions can be minimized. For example, pollutants with a short lifetime should be excluded to minimize the affect of changes in air mass composition caused by reactivity. Alternatively, if sources are close to the monitoring site, reaction times are minimized and it may be appropriate to include these species.

Ambient Data

CMB analyses were performed on 0500 PDT data collected at Bakersfield Golden State, Clovis, and Sacramento Del Paso. Laboratory uncertainty estimates were not provided and collocated sampling was not available to calculate method uncertainty. Fractional uncertainties have previously been calculated for toxic VOCs based on national collocated data giving an estimate of 15-20% uncertainty for VOCs (Brown et al., 2007; Wade et al., 2007). Data below detection were substituted with one-half of the method detection limit (MDL) and given an uncertainty of 5/6*MDL.

Fitting species were selected based on two measures: percent of data above the limit of detection (i.e., data quality) and reactivity (i.e., applicability for CMB). Only species that had a similar or greater lifetime than that of toluene (9h) were included, with the exception of isoprene and acetylene. Isoprene is a unique marker of biogenic emissions and acetylene is useful in differentiating among mobile source profiles. Species with greater than 70% of data below detection were also excluded. **Table 2** contains a summary of fitting species included in CMB analyses.

Table 2. Fitting species included in CMB by site.

(Page 1 of 2)

Parameter	Bakersfield	Clovis	Sacramento
1,2,4-Trimethylbenzene	*	*	*
2,2,4-Trimethylpentane	*	*	*
2,3-Dimethylbutane	*	*	*
2,3-Dimethylpentane	*	*	*
2-methylheptane	*	*	*
2-Methylhexane	*	*	*
2-Methylpentane	*	*	*
Acetylene	*	*	*
Benzene	*	*	*
Cyclohexane	*	*	*
Cyclopentane	*	*	*
Ethane	*	*	*
Ethylbenzene	*	*	*
Ethylene	*	*	*
Isobutane	*	*	*
Isopentane	*	*	*

Table 2. Fitting species included in CMB by site.

(Page 2 of 2)

Parameter	Bakersfield	Clovis	Sacramento
Isoprene		*	*
m/p - Xylene	*	*	*
Methylcyclohexane	*	*	*
n-Butane	*	*	*
n-Decane	*	*	*
n-Heptane	*	*	*
n-Hexane	*	*	*
n-Nonane	*		
n-Octane	*	*	*
n-Pentane	*	*	*
n-Undecane	*	*	
o-Xylene	*	*	*
Propane	*	*	*
Propylene		*	*
Toluene	*	*	*

Source Profiles

The most up-to-date compilation of California source profiles was obtained from the California Air Resources Board (ARB) database (U.S. Environmental Protection Agency, 2006). The profiles were originally normalized to TOG, and were re-normalized to the sum of PAMS target compounds. While the ARB database covers a wide range of sources, it lacks a diesel source profile. Additional source profiles, including diesel, were obtained from Watson's review (2001) of CMB on VOCs.

Uncertainty estimates were provided with the Watson source profiles, but were not provided in the ARB database. In CMB analysis of California VOC data, Fujita et al (1995), started with an uncertainty of 20% for species estimated to be well above detection ($>0.1\%$ of profile), while a more advanced technique was used for species constituting $<0.1\%$ of the profile. In this work, a blanket uncertainty of 20% was used for species that were $>0.1\%$ of the profile and 40% was used for species likely to be closer to the detection limit, with a contribution of $<0.1\%$. Mobile source profiles measured before 1996 were excluded from the analysis due to RFG changes that occurred in California in 1995. Mobile and non-mobile source profiles used in this analysis are shown in the Attachment.

Methodology

The general CMB approach used in these analyses is similar to that of Watson et al (2004). Using an iterative process, many source profile "sensitivity" tests were performed to arrive at the most statistically sound result. Each sensitivity test has a different purpose; for example, the first sensitivity test was used to identify the most appropriate light-duty source profile using a subset of mobile tracer pollutants. Statistically, the "best" profile is indicated by a

high r^2 , a low Chi Square, and a reasonable mass apportionment. The results of the first sensitivity test at Bakersfield can be found in **Table 3**. The purpose of this test is to understand which combination of light- and heavy-duty source profiles provide the best fit for mobile tracer species. Using Bakersfield data, the mix of Watson heavy-duty and ARB light-duty source profiles provides mediocre results and unlikely mass apportionment, with heavy-duty apportioned as a higher percent of the mass than light-duty (Table 3, rows 2 through 8). The Watson light-duty profile, on the other hand, gives excellent results: a significantly higher r^2 , and lower Chi squared, and reasonable mass apportionment (Table 3, last row), and is therefore used in final analyses.

Table 3. CMB sensitivity tests of various light-duty source profiles at Bakersfield.

Light-duty Profile	Heavy-duty Profile	R^2	Chi Square	Average Mass Apportioned	Average Mass Apportioned to Light-duty	Average Mass Apportioned to Heavy-duty
Catalyst - stabilized exhaust - ARB summer 1997	Watson ^a	0.80	6.82	17%	8%	9%
Catalyst - stabilized exhaust - ARB summer 1998	Watson ^a	0.80	6.81	17%	8%	9%
Catalyst - stabilized exhaust - ARB summer 1999	Watson ^a	0.80	6.81	17%	8%	9%
Catalyst - stabilized exhaust - ARB summer 2001	Watson ^a	0.80	6.81	17%	8%	9%
Catalyst - stabilized exhaust - ARB summer 2002	Watson ^a	0.80	6.81	17%	8%	9%
Catalyst - stabilized exhaust - ARB summer 2003	Watson ^a	0.80	6.81	17%	8%	9%
Cat start exhaust SSD etoh 2.0% - ARB 1996	Watson ^a	0.82	6.14	17%	8%	9%
Van Nuys tunnel emissions	Fujita ^b	0.96	1.39	30%	25%	5%

^a Tuscarora Tunnel (PA) heavy-duty emissions (Watson et al., 2001)

^b Fujita et al. (1997)

All other profiles from ARB (U.S. Environmental Protection Agency, 2006)

After light- and heavy-duty source profiles were selected, the next series of sensitivity tests was used to characterize the most appropriate mix of additional mobile source profiles including mobile evaporative emissions, liquid gasoline, and non-stabilized exhaust. Additional sensitivity tests investigated the systematic inclusion of other source profiles (e.g., industrial and biogenic emissions) to arrive at the most statistically sound mix of sources at a site. Additionally, the usefulness of including tracer species that had a high percentage of data below detection (e.g., n-nonane) was tested. In the end, nearly 100 systematic CMB runs were used to arrive at the final result.

While there is confidence in the CMB analyses, results are limited by source profile availability and accuracy as well as inherent model assumptions. Because source profiles were not collected at the monitoring sites, existing sources may not be characterized due to the lack of

appropriate source profiles. These profiles are likely a fair approximation to the mix of sources at these sites.

Results by Site

Table 4 provides a statistical breakdown of CMB results by site. R-square is a measure of the fraction of variance in measured concentrations that is explained by the variance in calculated concentrations. Higher R-square values indicate better agreement between measured and calculated data sets; a value greater than 0.8 is considered good agreement. Chi-square is the weighted sum of squares of the differences between calculated and measured fitting species concentrations. Lower chi-square values indicate better agreement between measured and calculated data. A chi-square value less than 1 indicates very good agreement and a chi-square between 1 and 2 is acceptable agreement (Coulter, 2004). R-square and chi-square results at all three sites show good agreement between measured and calculated data.

Table 4. Statistical measures of CMB results by site.

Site	Average R-square (Standard Deviation)	Average Chi-square (Standard Deviation)
Bakersfield	0.91 (0.06)	0.91 (0.5)
Sacramento	0.90 (0.03)	0.67 (0.3)
Clovis	0.91 (0.04)	0.80 (0.3)

Figure 9 summarizes CMB apportionment results by site (results by site and sample are shown in the Attachment). Unidentified mass is the difference between TNMOC and the sum of PAMS target compounds; this mass was not included in CMB analyses. Unapportioned mass is mass that was included in CMB analyses, but could not be accounted for using available source profiles. Unapportioned mass can be positive (i.e., under-apportionment) or negative (i.e., over-apportionment). The typical range of acceptable CMB mass apportionment is $100 \pm 20\%$ (Coulter, 2004); CMB results at the three sites were within this range.

At Bakersfield, mobile heavy-duty, mobile light-duty, evaporative, and liquid gasoline sources were identified, accounting for 45% of TNMOC mass. Industrial sources identified include coatings (8.9% of TNMOC) and refining (29% of TNMOC). The refining profile includes a large contribution from ethane and propane, which are also ubiquitous in the atmosphere due to oxidation pathways. This profile, therefore, also picks up the aged VOC fraction, which is why it is so large. A biogenic factor was not identified at Bakersfield because 78% of isoprene measurements were below detection. When isoprene was above detection, its concentration was less than 1% of TNMOC.

At Sacramento, mobile heavy-duty, mobile light-duty, and evaporative sources were identified accounting for 42% of TNMOC mass. Industrial sources include coatings (9.6% of TNMOC) and refining/aged (11% of TNMOC). Biogenic emissions account for 0.35% of the total mass.

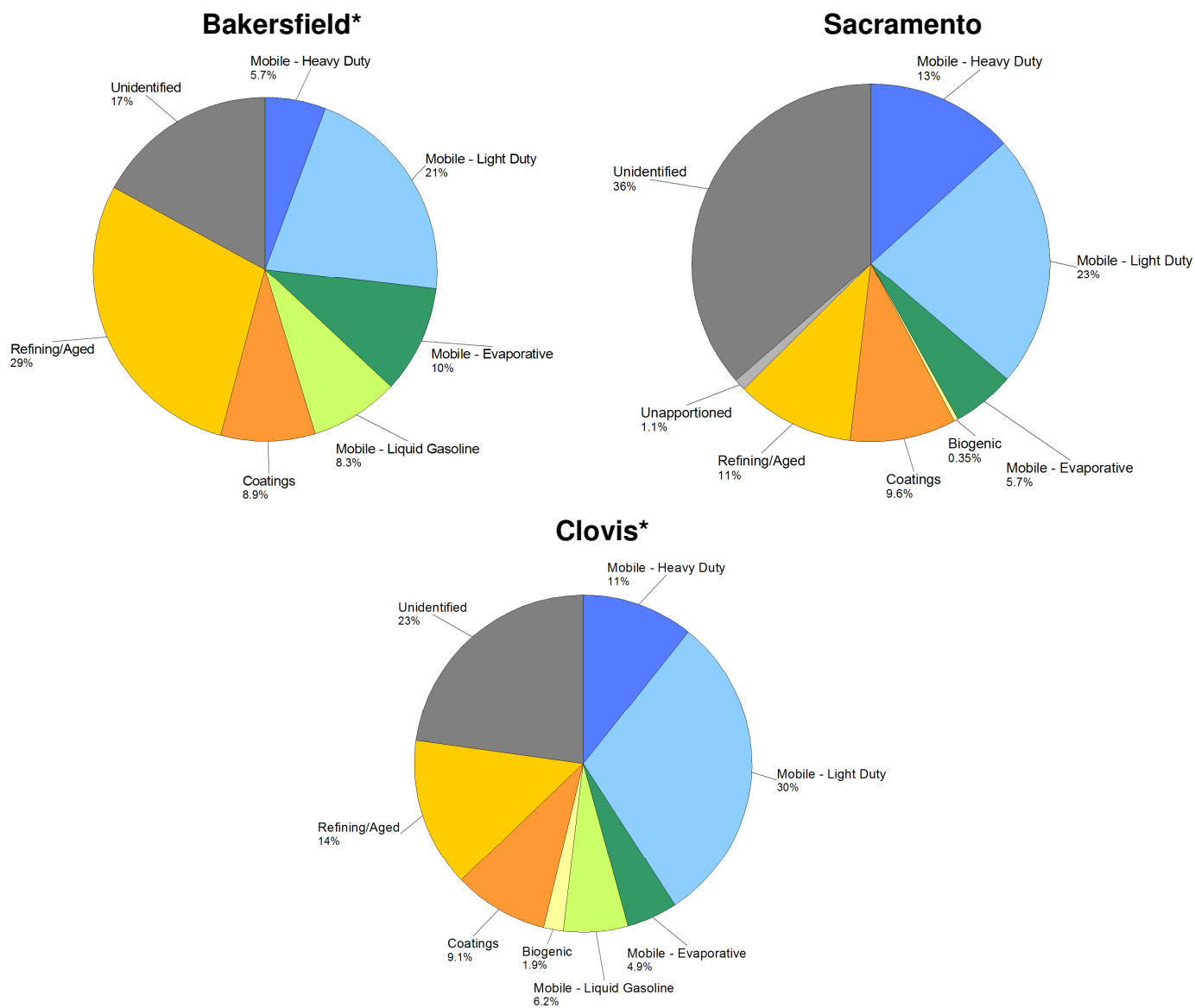


Figure 9. Average relative contribution of CMB profiles to the total mass. Unapportioned is mass that could not be accounted for by the source apportionment model. Unidentified mass is the difference between TNMOC and the sum of PAMS target compounds; this mass was not included in CMB. *Bakersfield and Clovis average unapportioned mass was -41 ppbC (12% of TNMOC) and -10 ppbC (4.3% of TNMOC), respectively.

At Clovis, mobile heavy duty, light duty, evaporative, and liquid gasoline sources were identified, accounting for 52% of TNMOC mass. Industrial sources include coatings (9.1% of TNMOC) and refining/aged (14% of TNMOC). Biogenic emissions account for 1.9% of TNMOC.

The average results by weekday versus weekend were compared to evaluate the CMB results (**Figure 10**). At Clovis and Bakersfield, the contribution of mobile light-duty sources is significantly lower on weekends compared to weekdays, especially for Clovis, the site most heavily dominated by mobile emissions. Sacramento CMB results do not show a difference in weekday and weekend mobile mass, which agrees with the small subset of year-2000 0500 PDT ambient data. This lack of decrease in mobile mass on weekends may account for the poorer agreement between ambient- and emission inventory-derived TNMOC/NO_x ratios on weekend days than on weekdays observed during the EI reconciliation (Chinkin and Reid, 2006). However, it should be noted that the larger data set of 1996–2000 0500 PDT ambient samples shows lower TNMOC mass on weekends compared with weekdays at Sacramento.

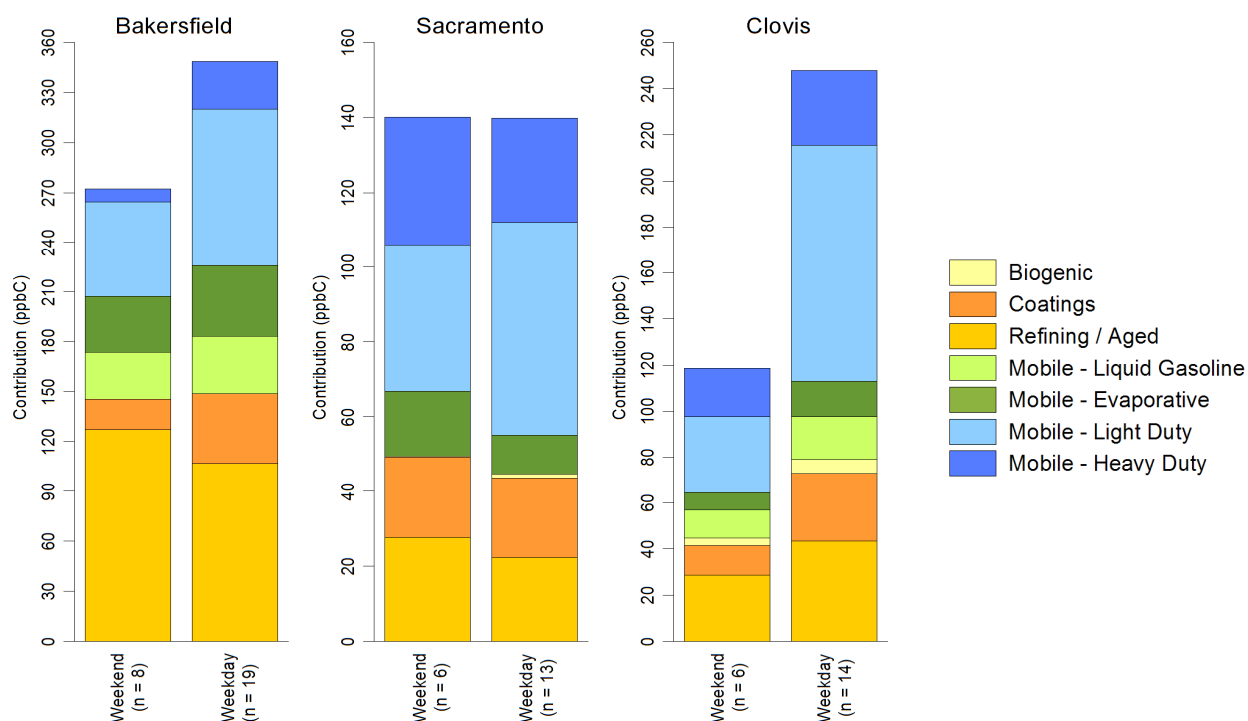


Figure 10. Average weekend and weekday CMB results by site.

Average results by wind quadrant were also produced for comparison to previous EI work (**Figure 11**). These averages were calculated using results for only a few days and should therefore be considered qualitative; the specific number of results included in each average is indicated in the figure label. Additionally, the ambient concentrations have an inverse relationship with wind speed, which may affect some results if winds from a given direction are typically slower than from other directions.

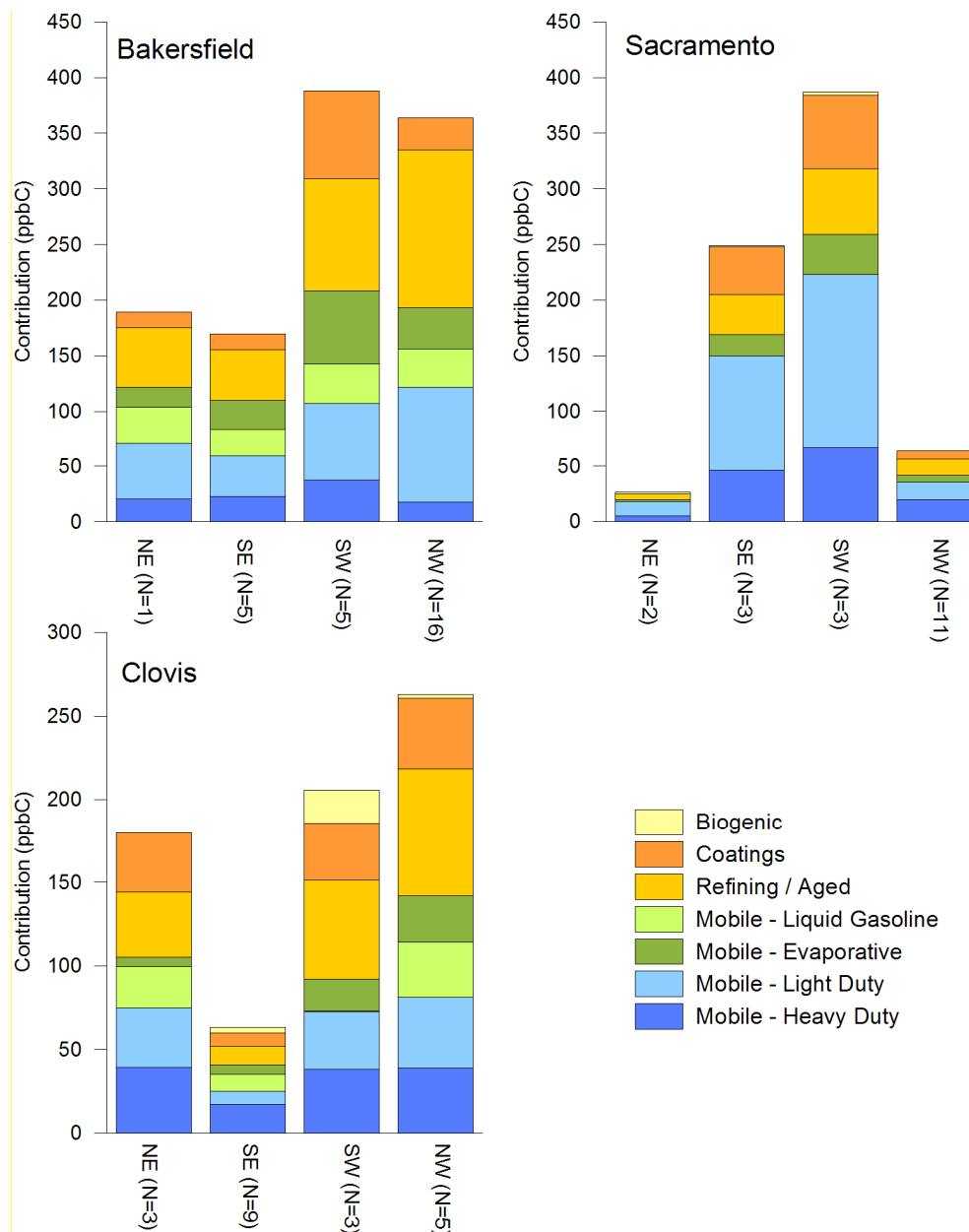


Figure 11. Average CMB results by wind quadrant. Averages were produced from a limited number of measurements, as indicated in the label.

Results show that mobile sources, including evaporative emissions, liquid/unburned gasoline and, light- and heavy-duty emissions, are a large amount of the ambient mixture at all sites. These mobile sources are significantly lower on weekends compared to weekdays at Clovis and Bakersfield, but show little difference between weekday and weekend contributions at Sacramento. The result at Sacramento agrees with the ambient data and is likely caused by a low number of samples. Despite the low number of samples, the allocation of source strength by wind quadrant may also be useful for refining EI estimates.

Positive Matrix Factorization (PMF) Analysis

PMF is a multivariate factor analysis tool that has been applied to a wide range of data, including speciated PM_{2.5} data, deposition data, air toxics data, and VOC data. The PMF input requires an ambient data set with associated uncertainties that are used to individually weigh each data point. Unlike CMB, source profiles are not included in the PMF input, rather PMF produces its own factor profiles based on variability in the ambient data set. PMF is described in detail elsewhere (Paatero, 1997; Paatero and Tapper, 1994).

The goal of multivariate receptor modeling such as PMF is to identify a number of sources that best characterize ambient data at a site, the source profiles, and the amount of mass contributed by each source to each individual sample (Watson et al., 1990; Watson et al., 1991; Henry et al., 1984). By individually weighing data, PMF allows missing or suspect data to be retained, and the analyst can adjust the uncertainty so that these data have a smaller impact on the final solution. The missing and below detection limit data are assigned much less weight compared with actual measured values, so these data are less important to the solution (Polissar et al., 2001; Hopke, 2003; Poirot et al., 2001; Ramadan et al., 2000; Lee et al., 2002; Song et al., 2001).

In this study, a standalone version of PMF (EPA PMF version 3.0) was used. EPA PMF is a graphical user interface that was based on the PMF model and solved using the multilinear engine as implemented in the program ME-2 (Paatero, 1999). EPA PMF operates in a robust mode, meaning that “outliers” are not allowed to overly influence the fitting of the contributions and profiles.

Uncertainties in the EPA PMF solution are estimated using a bootstrapping technique, which is a re-sampling method in which “new” data sets are generated that are consistent with original data; each data set is decomposed into profile and contribution matrices; and the resulting profile and contribution matrices are compared with the base run (Eberly, 2005). Instead of inspecting point estimates, this method allows the analyst to review the confidence intervals for each species over many runs to obtain more robust profiles.

Ambient Data and Uncertainties

PMF analyses were performed on data collected at Bakersfield, Clovis, and Sacramento between 1996 and 2000. Laboratory uncertainty estimates were not provided and collocated sampling was not available to calculate method uncertainty. Data above detection were included “as is” and given a fractional uncertainty of 20%. Data below detection were substituted with the MDL/2 and given an uncertainty of 5/6*MDL. Missing data were substituted with the median and given an uncertainty of 4*median.

Methodology

Like CMB, the general approach to obtaining reliable results from PMF is an iterative process. Many aspects can affect PMF results, including the input species, the number of factors, and extreme outlier data points. A series of tests were performed to arrive at the most statistically robust results based on the available data.

The first step was to choose parameters to be included in the model and assign their weighting. Parameter selection was based on data quality (i.e., percent of data above the detection limit) and co-linearity, as collinear species can artificially affect results. Parameters included in the model can also be designated as strong or weak, which affects the uncertainty in the ambient data. A parameter designated as strong will be included with the user-input uncertainty, while a parameter designated as weak will be included with three times the user-input uncertainty. A parameter is typically designated as weak based on the reliability of its data. For example, highly reactive species or species that are known to be poorly monitored should be designated as weak. One exception is isoprene, which is highly reactive, but is also a unique tracer for biogenic emissions, and was included as a strong species. **Table 5** contains a summary of parameters included in the final PMF model for the three sites.

Model performance criteria were used to guide the final solution in PMF, including the goodness-of-fit parameter (Q) and convergence statistics. Additionally, each PMF run was automatically replicated 10 times starting with different random locations (seeds), and the output compared. Stability in results among replicated runs is an important indicator in the quality of the results. Finally, the predicted results based on the combination of factors were compared to the input data. This includes examining the residuals for each species, the scatter plots between species, and the mass recovery. The species input into PMF, their weighting, and the number of factors was adjusted to arrive at the most statistically robust results. When the final solution was obtained, 300 bootstraps were run to quantify the error in output source profiles.

Table 5. Compounds and uncertainty weighting included in final PMF runs. S (strong) indicates a compound included with the original uncertainty, W (weak) indicates a compound included with three times the original uncertainty.

(Page 1 of 2)

Pollutant	Bakersfield	Clovis	Sacramento
1,2,4-Trimethylbenzene	S	S	S
2,2,4-Trimethylpentane	S	S	W
2,3-Dimethylbutane	W	W	W
2,3-Dimethylpentane	W	W	W
2-Methylpentane	W	W	S
3-Methylheptane	W		
3-Methylhexane	W	S	W
Acetylene	W	W	W
Benzene	S	S	S
Cyclohexane		W	W
Cyclopentane	W		
Ethane	S	S	S
Ethylbenzene	S	S	W
Ethylene	S	S	S
Isobutane	S	S	S
Isopentane	S	S	S
Isoprene		S	S

Table 5. Compounds and uncertainty weighting included in final PMF runs. S (strong) indicates a compound included with the original uncertainty, W (weak) indicates a compound included with three times the original uncertainty.

(Page 2 of 2)

Pollutant	Bakersfield	Clovis	Sacramento
M_P Xylene	S	S	S
Methylcyclohexane	S	W	S
Methylcyclopentane	W	S	S
M-Ethyltoluene	W	S	W
N-Butane	S	S	S
N-Decane		W	W
N-Heptane	S	S	W
N-Hexane	S	S	S
N-Octane	W		
N-Pentane	S	S	S
Propane	S	S	S
Propylene	W	W	W
Toluene	S	S	S
Sum of PAMS Target Compounds	W	W	W

Results by Site

Figures 12 through 14 contain PMF bootstrapped profiles by site. The goal is to have a small interquartile range around the original profile value indicating good agreement among the 300 bootstraps. Species that were given higher uncertainty or were below detection for a large fraction of the total samples are expected to have larger variability in their apportionment. The PMF analysis is limited by the precision of the data and the availability of unique source tracers, similar to CMB. For example, n-undecane had a large fraction of data below detection at all sites, and was therefore not included in the model input. Loss of these species made it difficult for PMF to resolve a heavy-duty mobile source profile, because this species is typically used as a tracer. Additionally, isoprene measurements at Bakersfield had too much data below detection to include in PMF analysis, therefore a biogenic profile was not resolved. As mentioned previously, isoprene measurements that were above the limit of detection accounted for less than 1% of TNMOC at Bakersfield. Overall mobile sources were resolved and had the largest contribution to mass at all sites, along with some combination of aged air, industrial emissions, solvent usage, or biogenic emissions. Additional samples and better precision may help resolve other sources.

At Bakersfield, three factors gave the best solution, accounting for the total mass well and representing mobile exhaust (combined light- and heavy-duty), evaporative and liquid/unburned gasoline, and refinery/industrial/aged. Mobile sources were identified using the typical suite of tracer species used in CMB, such as acetylene and benzene for mobile exhaust, pentanes for liquid gasoline/evaporative, and ethane/propane for refinery/industrial emissions. Similar to

CMB, mobile sources accounted for about half of the mass. Unidentified mass was about 20%, and industrial or aged air comprised the remaining mass (see **Figure 15**).

At the Sacramento site, five factors were identified, and while within tolerance, the amount of unapportioned mass was somewhat high (14%). Mobile sources accounted for about 30% of the mass, industrial and aged air accounted for another 20% of mass, and 36% of the mass was unidentified (see Figure 15). The total contribution from industrial and coatings sources is similar between PMF and CMB, though the PMF mobile factor is lower likely due to the high amount of unapportioned mass with PMF. Because the non-mobile apportionment was similar between the two analyses, this gives us confidence that, similar to Bakersfield, mobile sources are a large amount of the mass and are likely under-represented in the EI.

Clovis showed similar results to the other sites and similar contributions between PMF and CMB; four factors were identified with PMF including mobile, industrial/aged, and minor contributions from solvent/coatings and biogenics. Average contributions from mobile and non-mobile sources were similar between PMF and CMB, with mobile sources about 50% of the mass, non-mobile sources about 25%, and another 23% of mass that could not be chemically identified (see Figure 15).

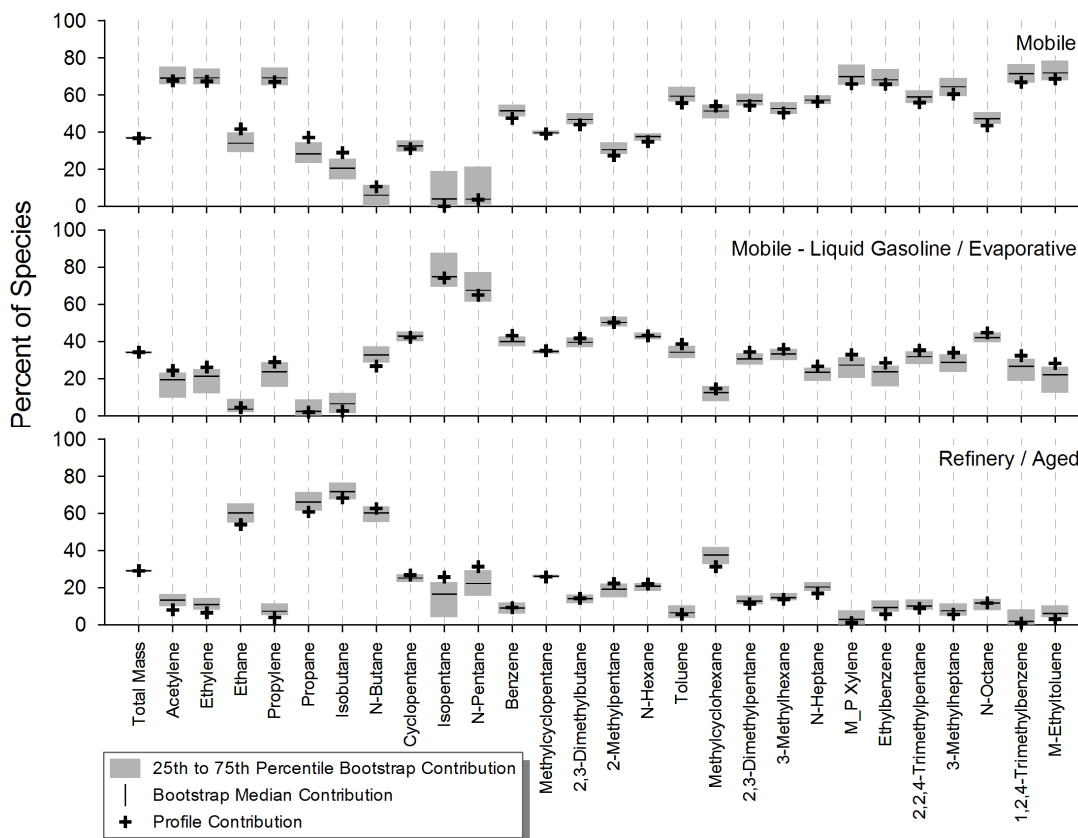


Figure 12. Bakersfield PMF bootstrap profile. Total mass is the sum of PAMS target compounds.

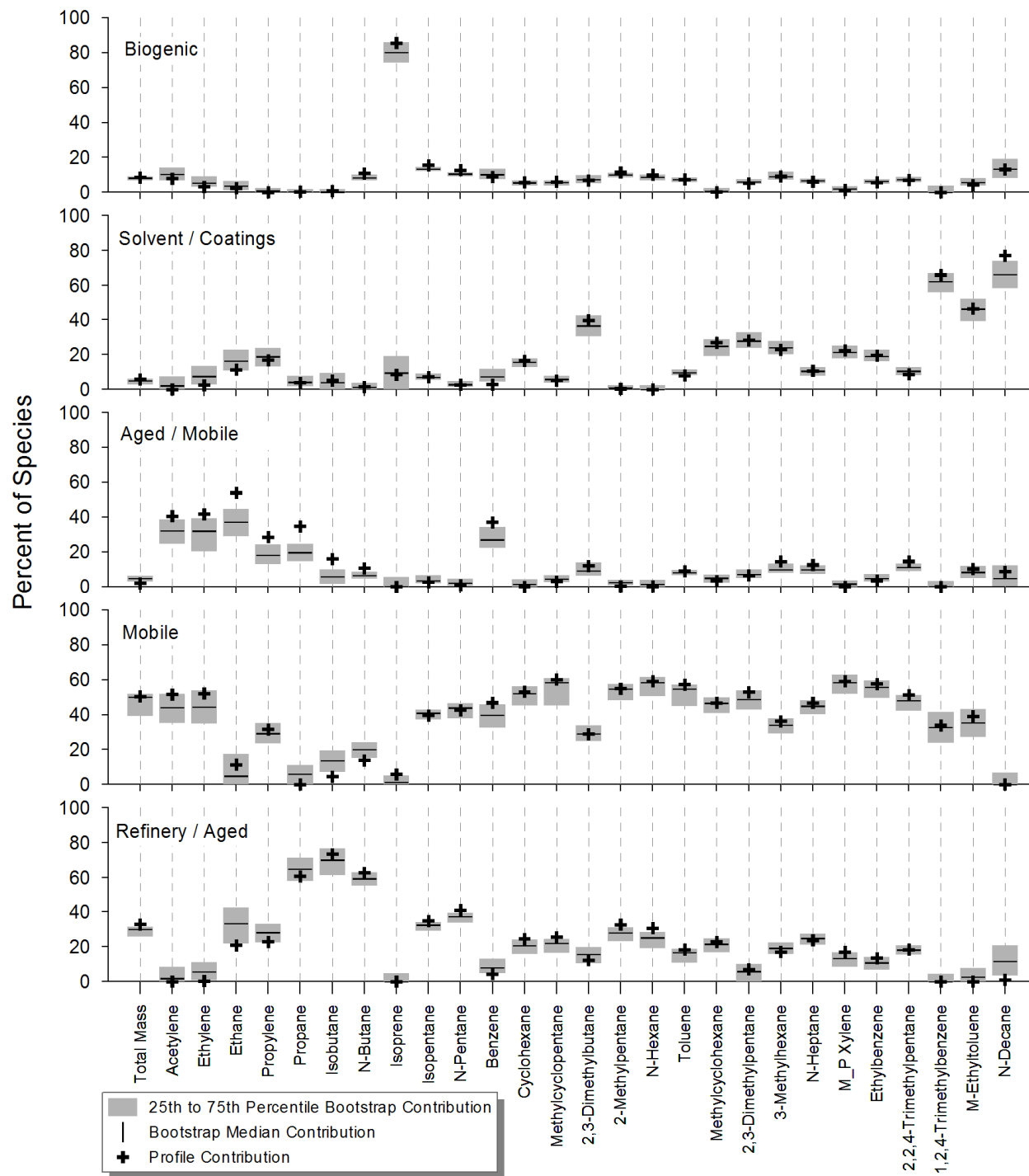


Figure 13. Sacramento PMF bootstrap profile. Total mass is the sum of PAMS target compounds.

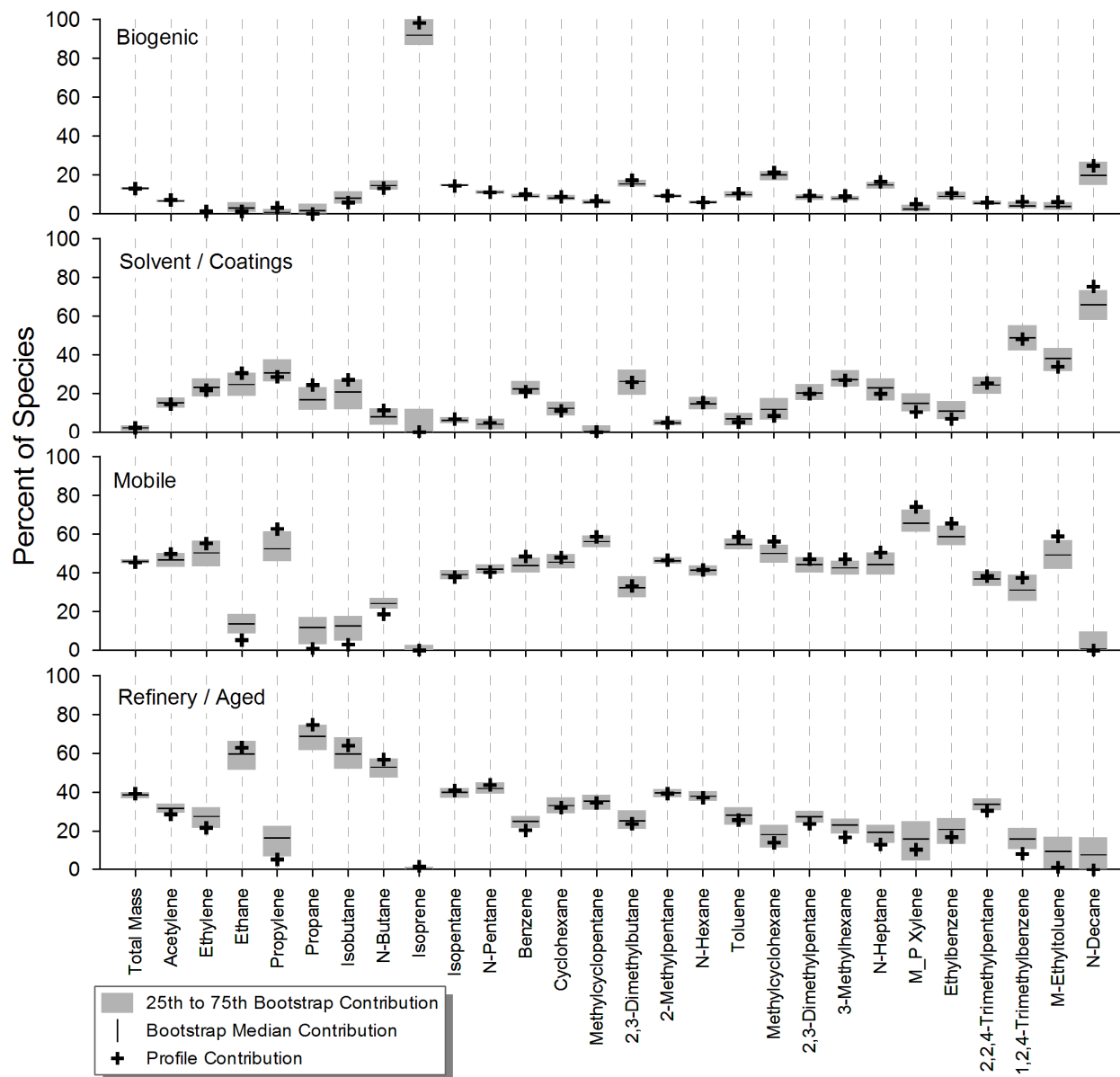


Figure 14. Clovis PMF bootstrap profile. Total mass is the sum of PAMS target compounds.

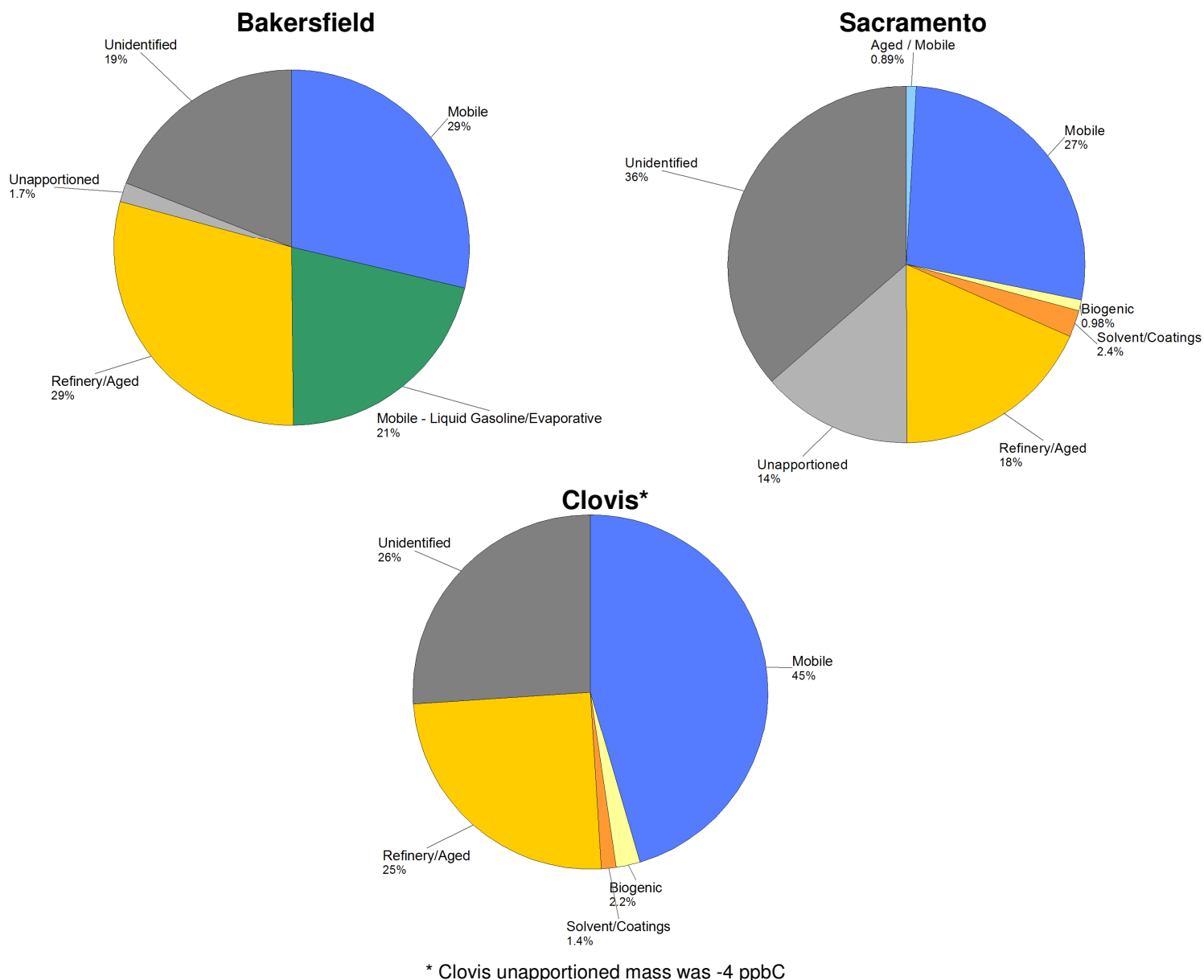


Figure 15. Relative contribution of PMF profiles to the total mass. Unapportioned is mass that could not be accounted for by the source apportionment model. Unidentified mass is the difference between TNMOC and the sum of PAMS target compounds; this mass was not included in PMF.

The average results by weekday versus weekend were compared to evaluate the PMF results (**Figure 16**). At Bakersfield and Clovis, the contribution of mobile sources is significantly lower on weekends compared with weekdays, especially for Clovis, the site most heavily dominated by mobile emissions. Sacramento PMF results do not show a large difference in weekday and weekend mobile mass, which is in agreement with year-2000 0500 PDT ambient samples, and with CMB. Investigation of all Sacramento 0500 PDT PMF results (N ~ 150) from

1996 to 2000 show a consistent contribution from all sources except mobile on weekdays and weekends. Mobile contributions are more than two times higher on weekdays than weekends, which agrees with the conceptual model of weekday/weekend emissions sources.

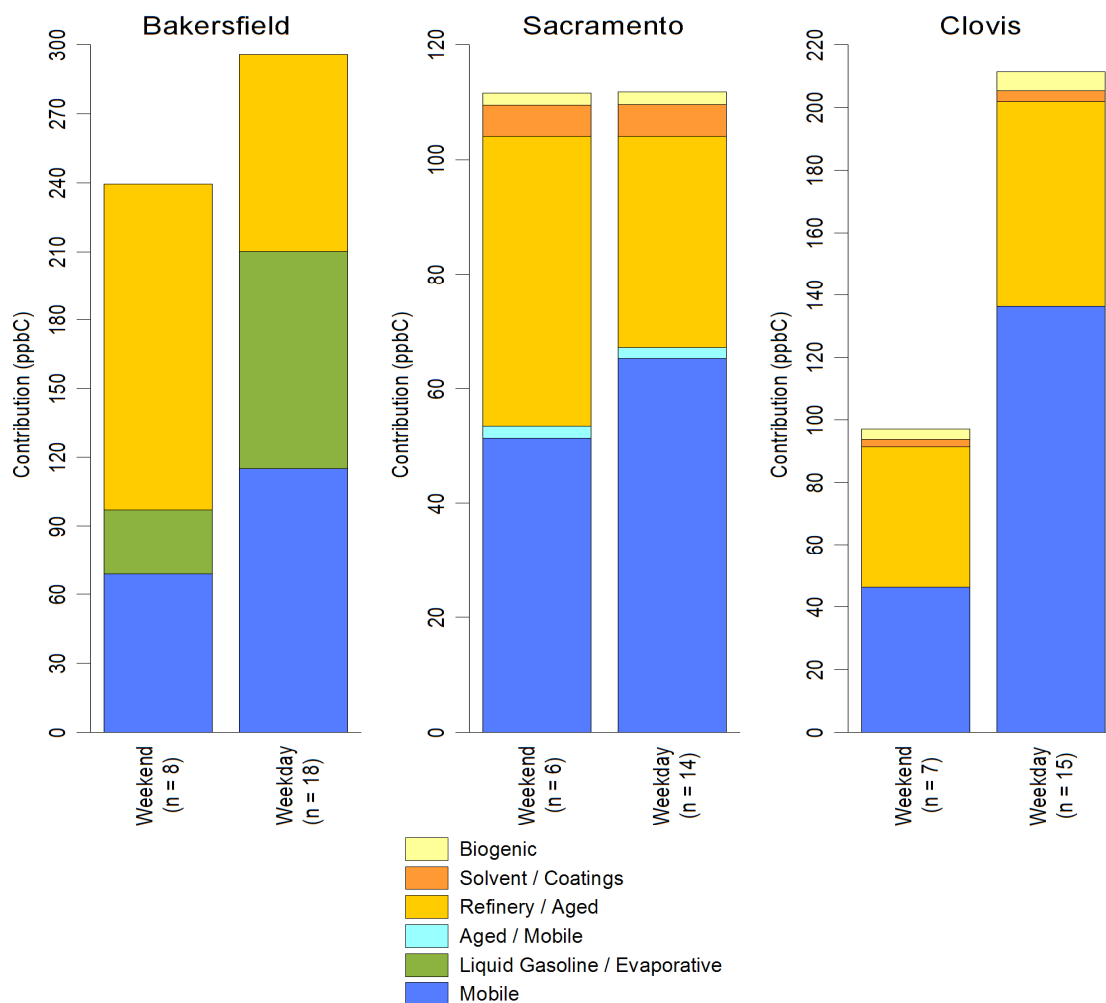


Figure 16. Average weekend and weekday PMF results by site.

Average results by wind quadrant were also produced for comparison to previous EI work (**Figure 17**). These averages were calculated using results for only a few days and should therefore be considered qualitative; the specific number of results included in each average is indicated in the figure label. Additionally, the ambient concentrations have an inverse relationship with wind speed, which may affect some results if winds from a given direction are typically slower than from other directions.

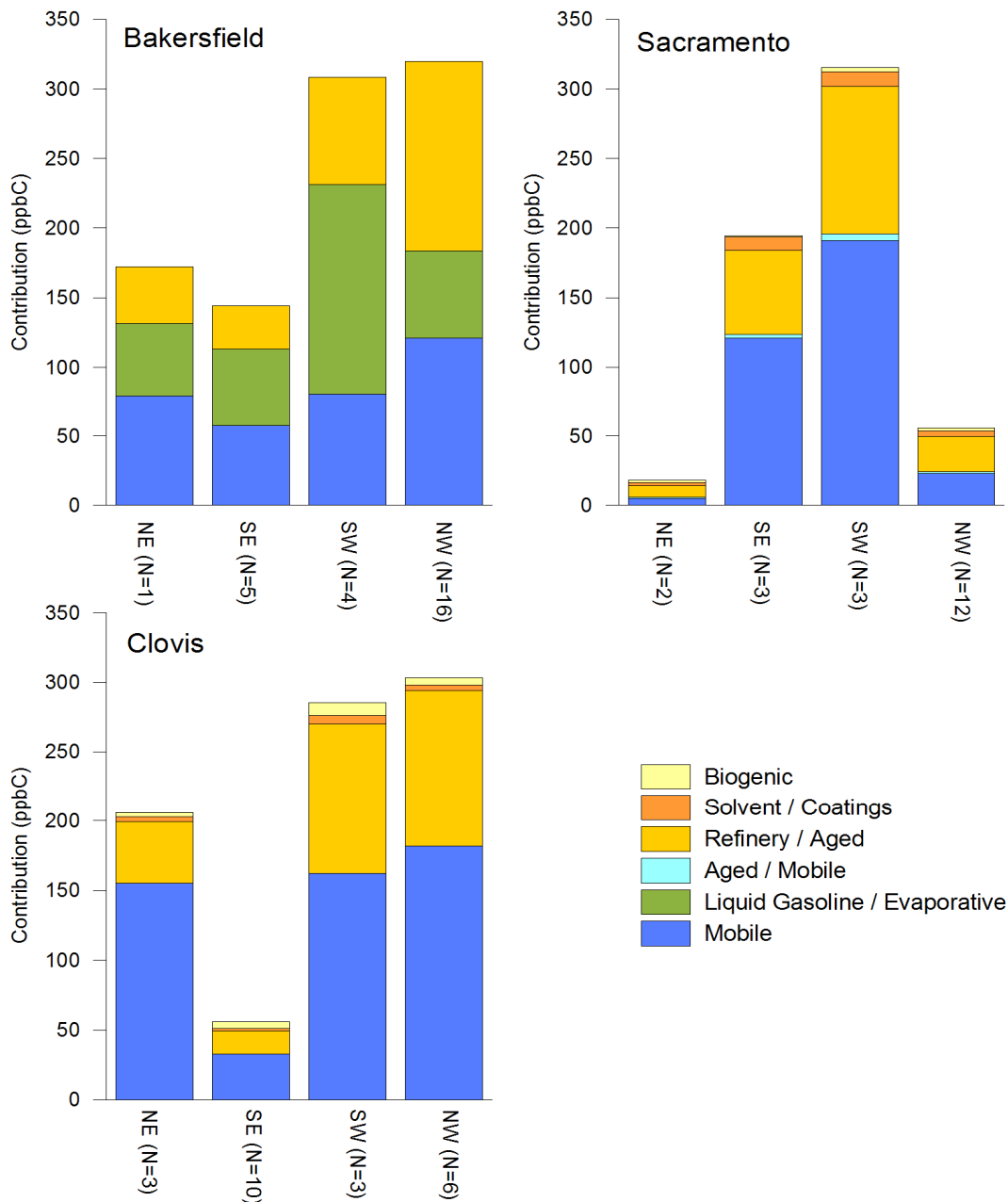


Figure 17. Average PMF results by wind quadrant. Note that some averages were produced from very few measurements as indicated in the label.

Summary of Integrated Findings

Overall results between CMB and PMF were similar (**Figure 18**) demonstrating that mobile sources account for 40-50% of the mass, non-mobile sources are between 20% and 40% of the mass, and biogenic emissions are small. Unidentified mass, determined analytically, was

between 17% and 36% of the mass.⁴ The similarity in results between the models gives more confidence to the results than if only one model had been used, because both models have complementary strengths and weaknesses. In addition, the similarity in results is encouraging given limitations in the original data. Using data with more precision, that are more representative of a variety of wind directions and speeds, and with a higher number of samples would further refine these results if needed.

Among the three Tier 1 sites, ambient TNMOC concentrations were highest at the Bakersfield site, exceeding TNMOC concentrations at the Sacramento and Clovis sites by about 75% and 45%, respectively (see Figure 15). However, the TNMOC emission inventory for the grid analysis zone around each monitoring site shows that TNMOC emissions are lowest at the Bakersfield site and highest at the Sacramento site (see **Figure 19**). Because the EI reconciliation work showed relatively good agreement between the EI and ambient data at the Sacramento site (Chinkin and Reid, 2006), this finding indicates that the overall TNMOC inventory is likely to be underpredicted at both the Clovis and Bakersfield sites.⁵

At the Sacramento site, PMF and CMB provided similar results overall when examining the 0500 PDT year-2000 ambient VOC data. The majority of TNMOC was determined to be contributed by mobile sources or was unidentified by the chemical analysis (the relative amount of unidentified mass is highest in Sacramento compared with Clovis and Bakersfield). When the breakdown of identified TNMOC from the source apportionment analyses was plotted against results from the EI, the mobile source contribution in the EI (61%) fell within the range of mobile source TNMOC contributions from the PMF (50%) and CMB analyses (66%), as shown in **Figure 20**. The contribution of biogenic emissions to TNMOC was higher in the EI than in the source apportionment analyses, which may be due to the fact that biogenic emissions are highly reactive and often present in concentrations that are below the detection limit of ambient monitoring equipment. Alternatively, this finding may result from a bias in the biogenic emissions model used to develop these emission estimates. Overall, these results corroborate the findings from the EI reconciliation work, which indicated that the EI and ambient data showed relatively good agreement at the Sacramento site.

Clovis showed a mediocre agreement between EI and ambient data comparisons. The EI apportions almost 60% of TNMOC emissions to stationary sources, while CMB and PMF results indicate that at least half of the mass is mobile in origin, with an additional 20% unidentified (non-mobile sources were only a quarter of the mass). When only the identified portion of the TNMOC mass is considered, the CMB/PMF results suggested that over 60% of the identified TNMOC mass is mobile in origin (see **Figure 21**). An adjustment of the EI to reflect more mobile source influence would likely result in better agreement between the EI and ambient data at Clovis.

At Bakersfield, the EI compared poorly with the ambient data, with ambient-derived TNMOC/NO_x ratios being three to four times higher than emission inventory-derived ratios

⁴ This unidentified mass could potentially be associated with specific sources based on an evaluation of tracer species trends, but significant effort outside the scope of this project would be required to be more specific.

⁵ It should be noted that other factors may influence the relationship between TNMOC emissions and concentrations at a given monitoring site, such as the reactivity of hydrocarbon species emitted and meteorological conditions.

(Chinkin and Reid, 2006). The EI shows less than half of the TNMOC attributed to mobile sources, while the CMB/PMF results suggest mobile sources account for 55% to 61% of the identified TNMOC mass (see **Figure 22**). These results suggest that mobile sources are under-represented in the EI around the Bakersfield site, though stationary source emissions are likely to be under-estimated as well, given the relatively low TNMOC emissions associated with this site.

These results indicate that TNMOC emissions are under-estimated at Bakersfield (and possibly Clovis), which may influence photochemical modeling results for those locations. In addition, mobile sources appear to be under-represented in the EI at Clovis and Bakersfield. Because the relative abundance of specific VOC species is different between mobile and non-mobile sources, especially with regard to ozone formation capability, these discrepancies suggest photochemical modeling results may not compare well with observed ozone concentrations in the Fresno (i.e., Clovis) and Bakersfield areas.

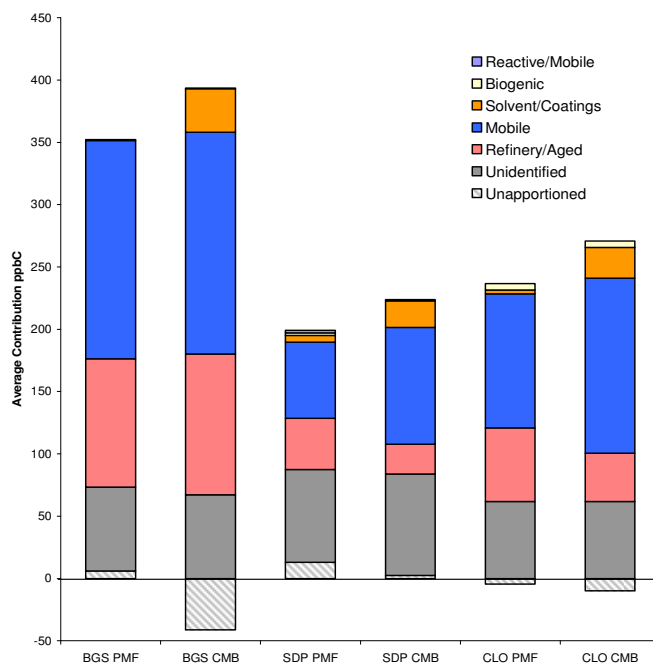


Figure 18. Summary of CMB and PMF analyses by site for 3-hr summer VOC samples at 0500 PDT in 2000. PMF analyses were conducted using 1996-2000 data to provide a large enough data set to perform reasonable analyses; only the 0500 PDT samples in 2000 are shown. Mass that could not be accounted for by the source apportionment model is unapportioned mass; a negative value indicates over-apportionment. Unidentified mass is the difference between TNMOC and the sum of PAMS target compounds; this mass was not included in the source apportionment models.

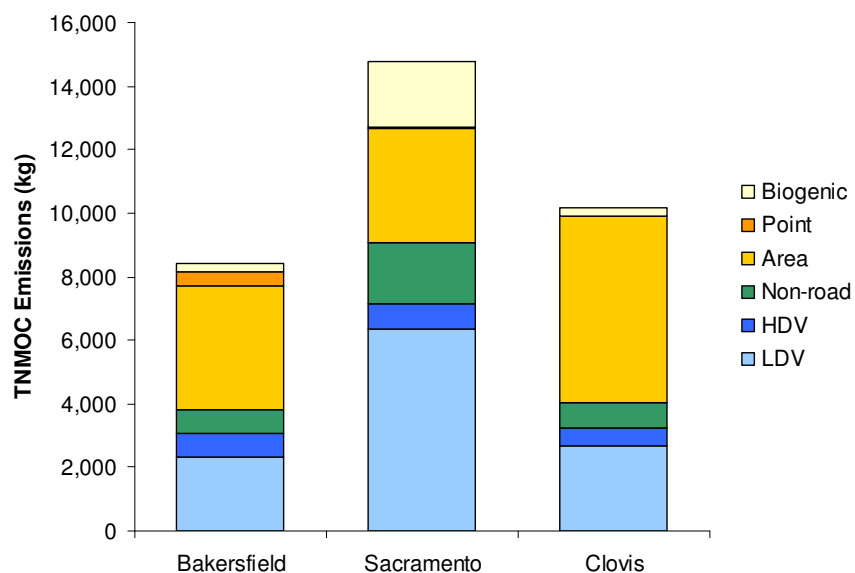


Figure 19. Summary of 0500 to 1000 PDT TNMOC emissions from the EI by source category.

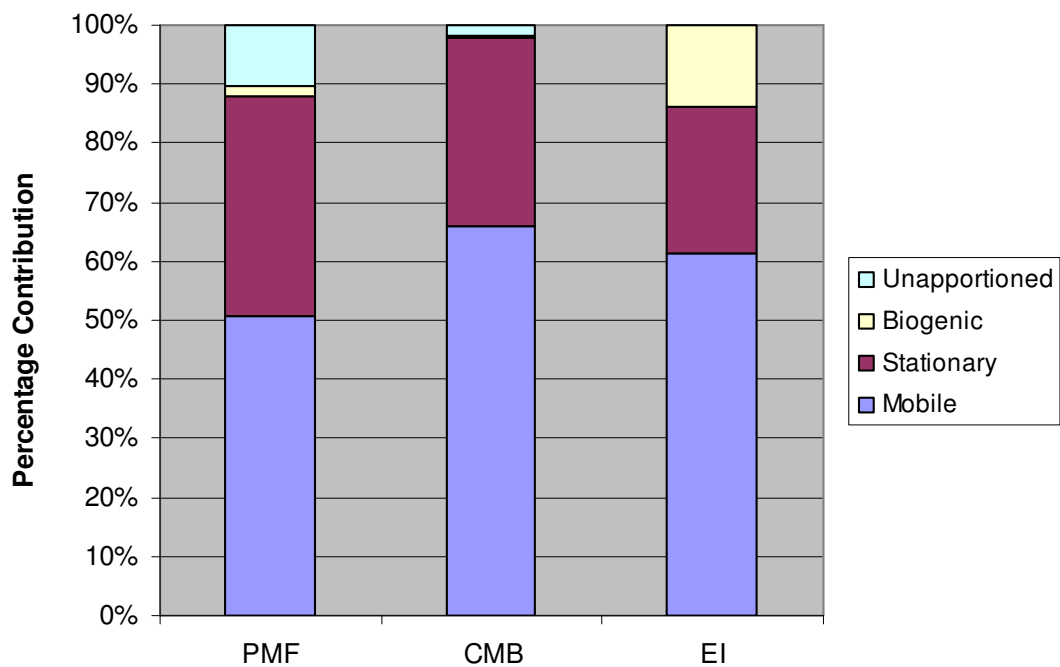


Figure 20. Comparison of source contributions to 0500 to 1000 PDT TNMOC at the SDP site from source apportionment analyses and the EI.

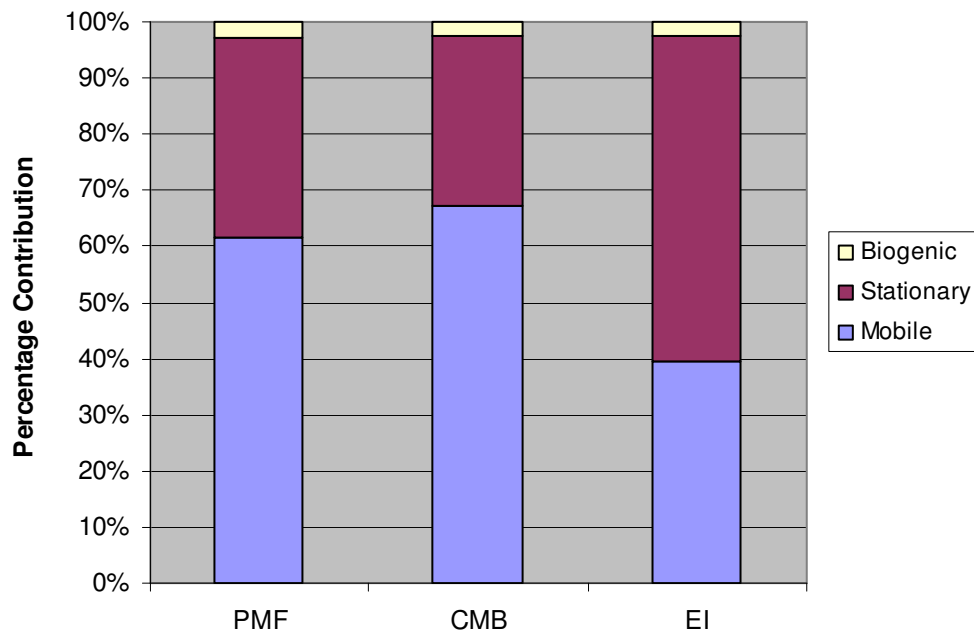


Figure 21. Comparison of source contributions to 0500 to 1000 PDT TNMOC at the CLO site from source apportionment analyses and the EI.

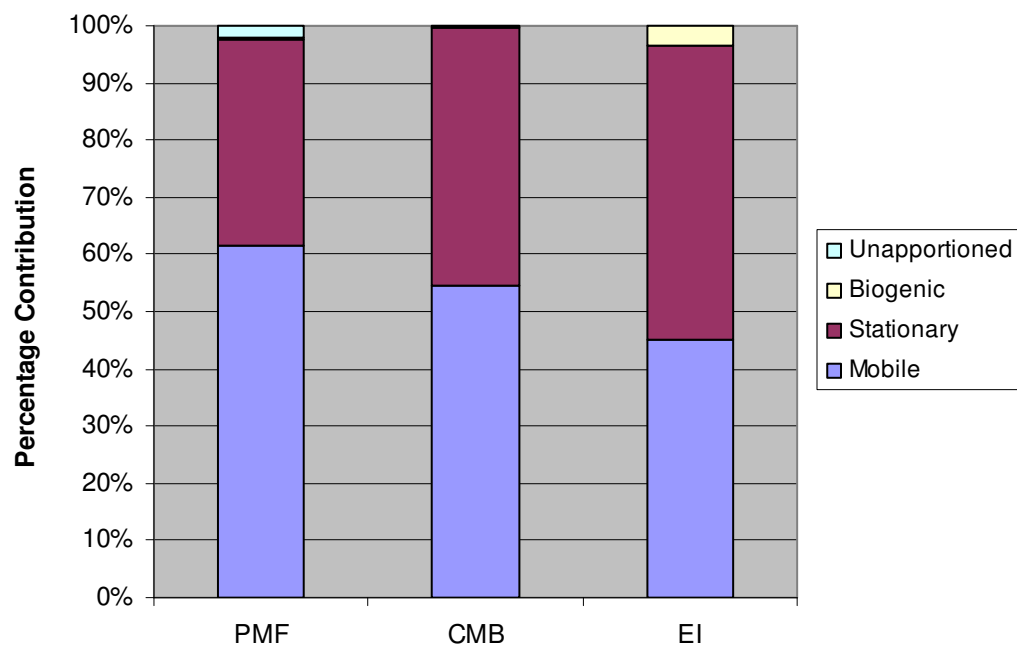


Figure 22. Comparison of source contributions to 0500 to 1000 PDT TNMOC at the BGS site from source apportionment analyses and the EI.

RECOMMENDATIONS

These analyses show that, as expected, discrepancies exist between the source mixture indicated in the EI and the ambient TNMOC data. Mobile sources appear to be under-predicted at the Bakersfield and Clovis sites. As a first approximation, the relative ratio of mobile to other sources could be adjusted so that mobile sources make up at least half the emissions. Total emissions were also not consistent with ambient data. The ambient concentrations at Bakersfield are nearly twice those at other sites, yet are the lowest total TNMOC emissions in the EI. If further refinement of the ambient data analyses is desired, additional years of data with better precision could be used. These additional years of data could also indicate trends over a longer time period, which could be compared to predicted trends in emissions.

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ATTACHMENT

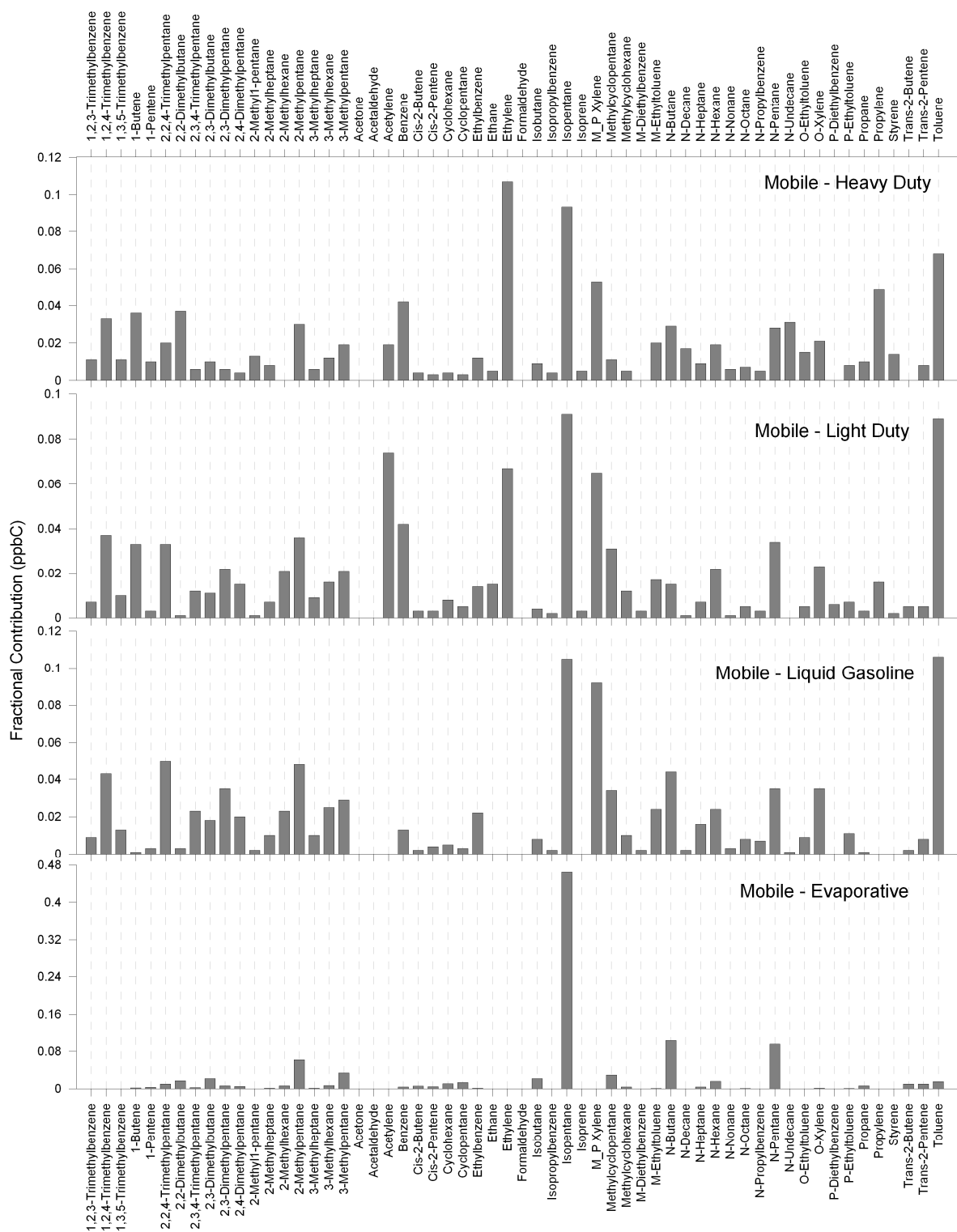


Figure A-1. CMB mobile source profiles.

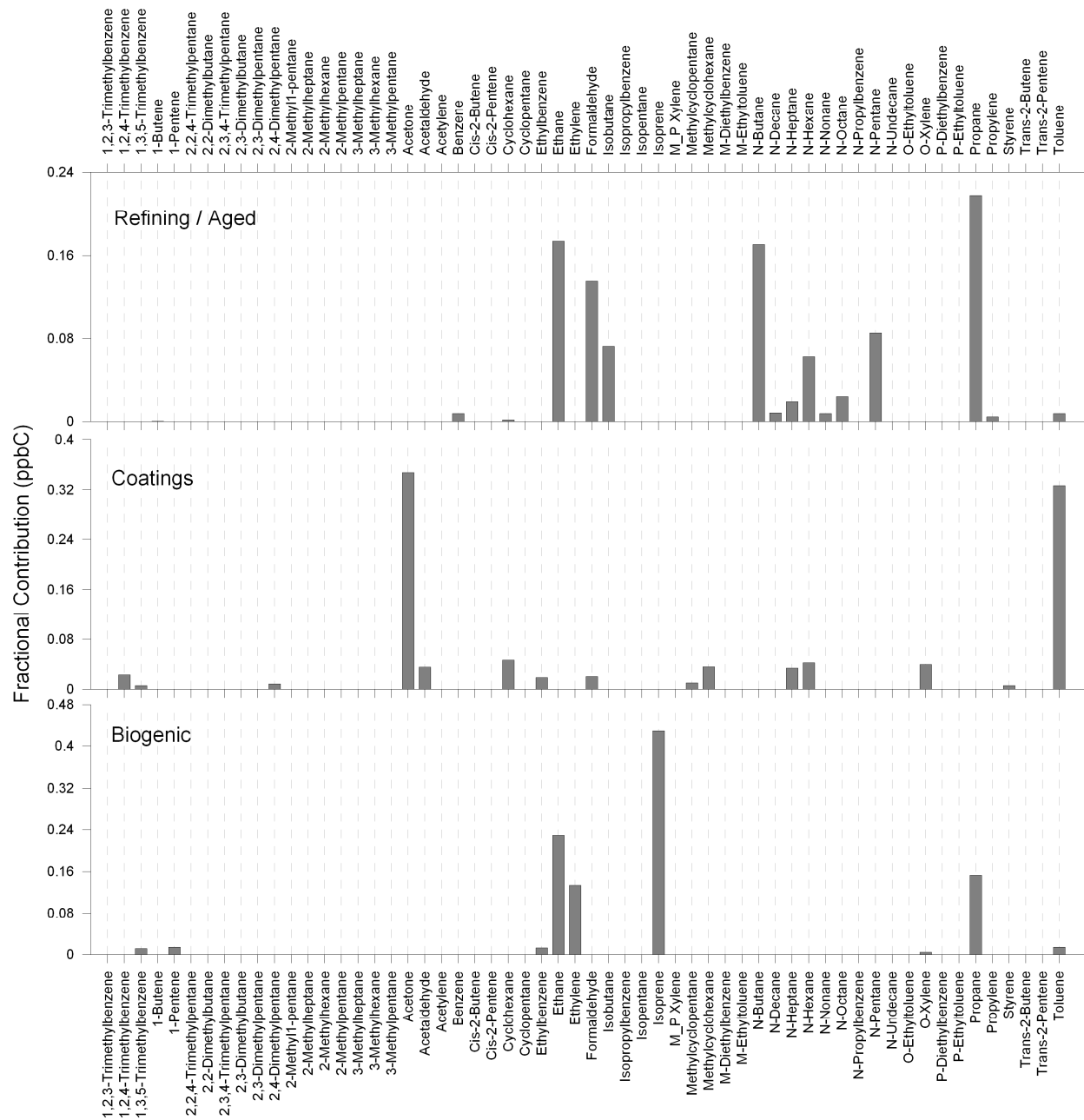


Figure A-2. CMB non-mobile source profiles.

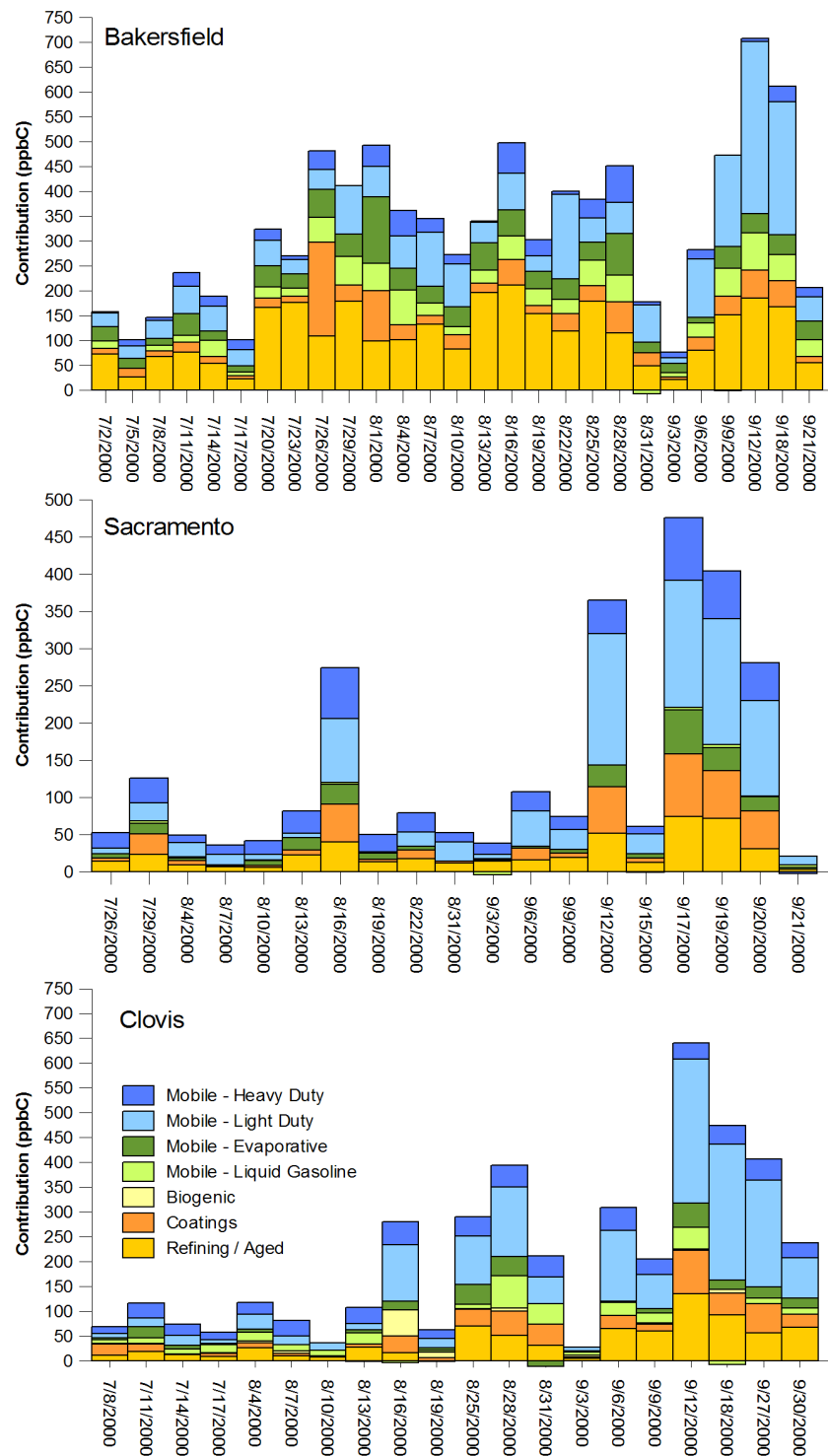


Figure A-3. CMB results by sample and by site.

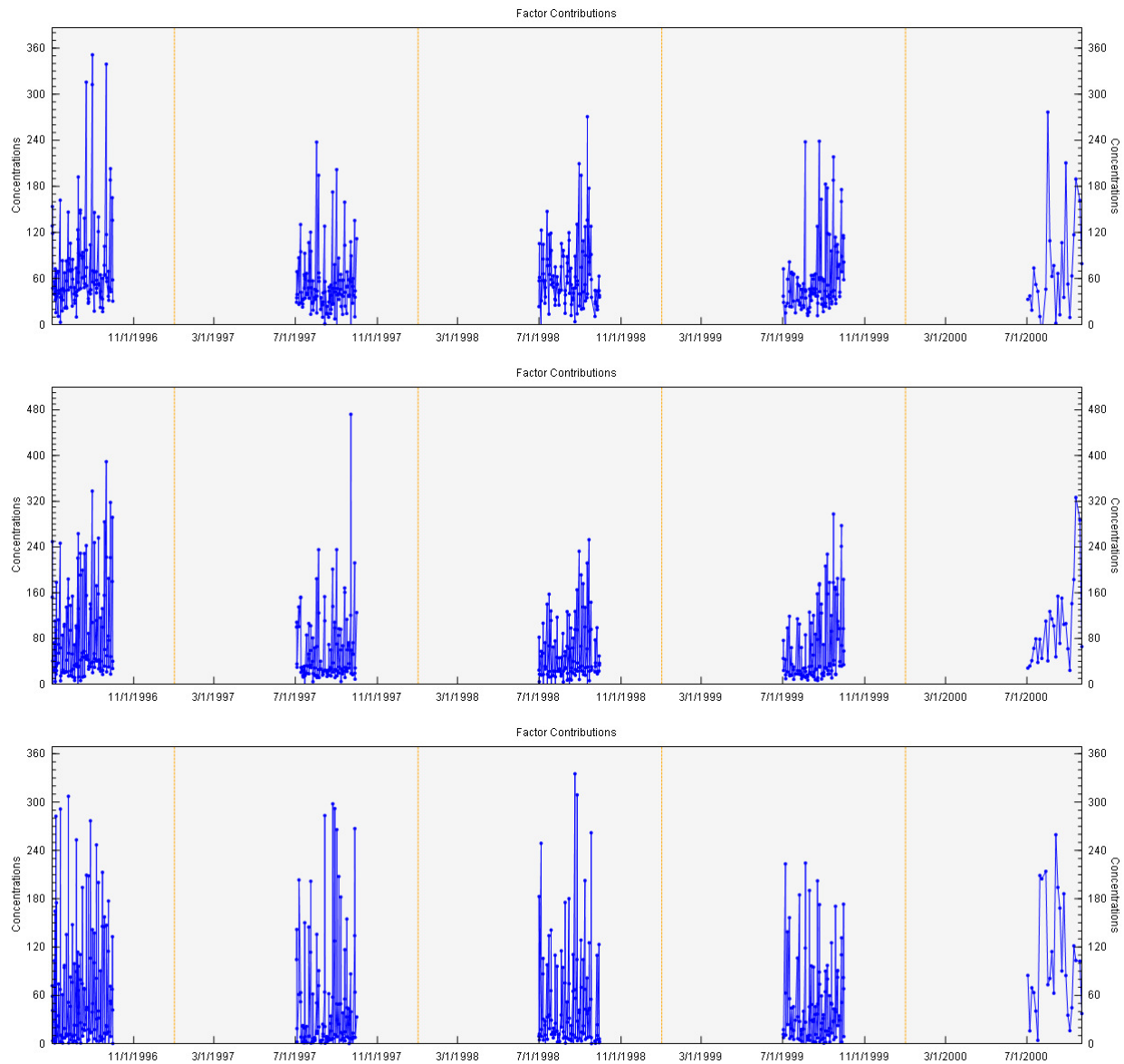


Figure A-4. Bakersfield PMF factor contributions. From top to bottom: mobile, refining/aged, mobile-liquid gasoline/evaporative.

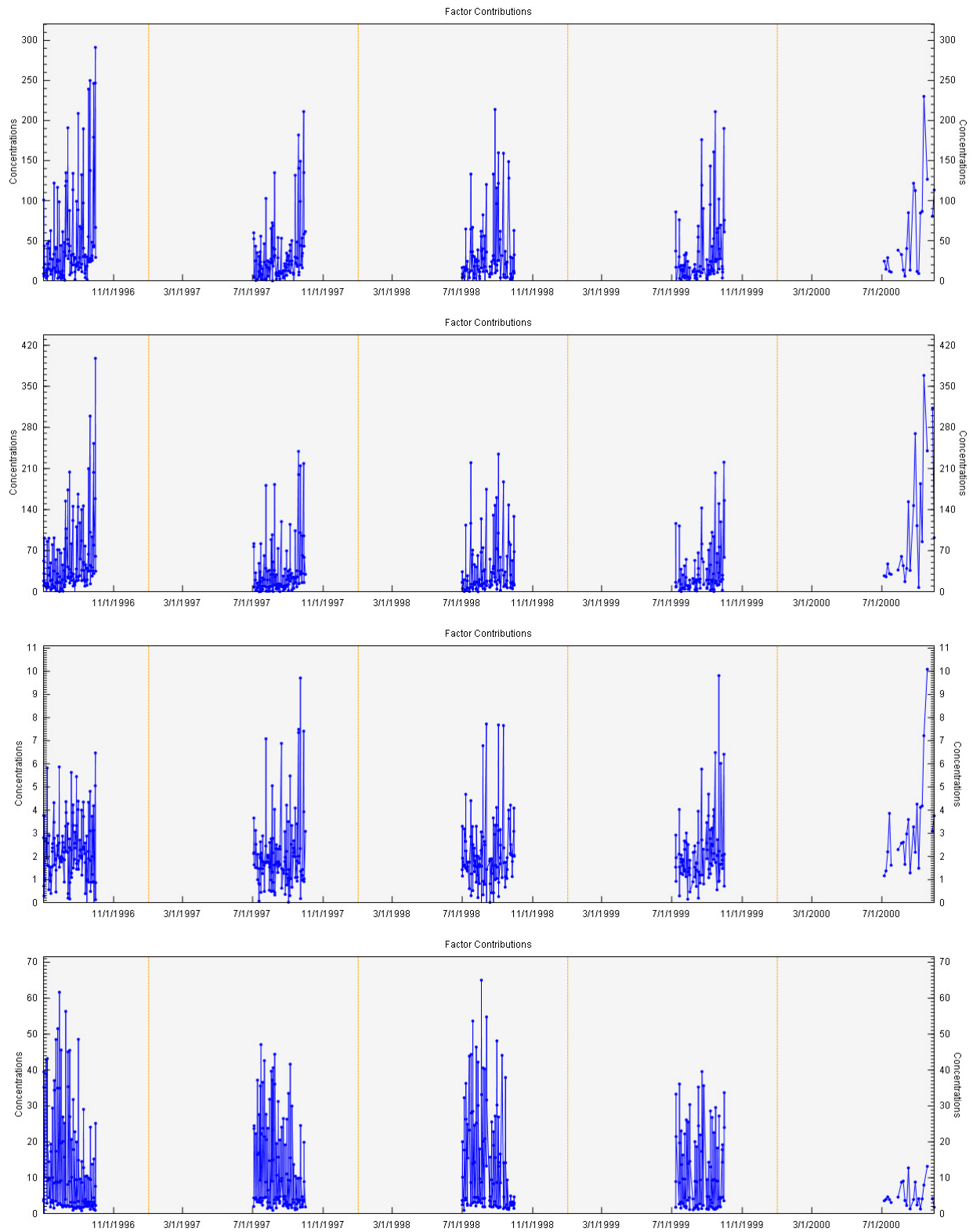


Figure A-5. Clovis PMF factor contributions. From top to bottom: mobile, coatings, biogenic, refining/aged.

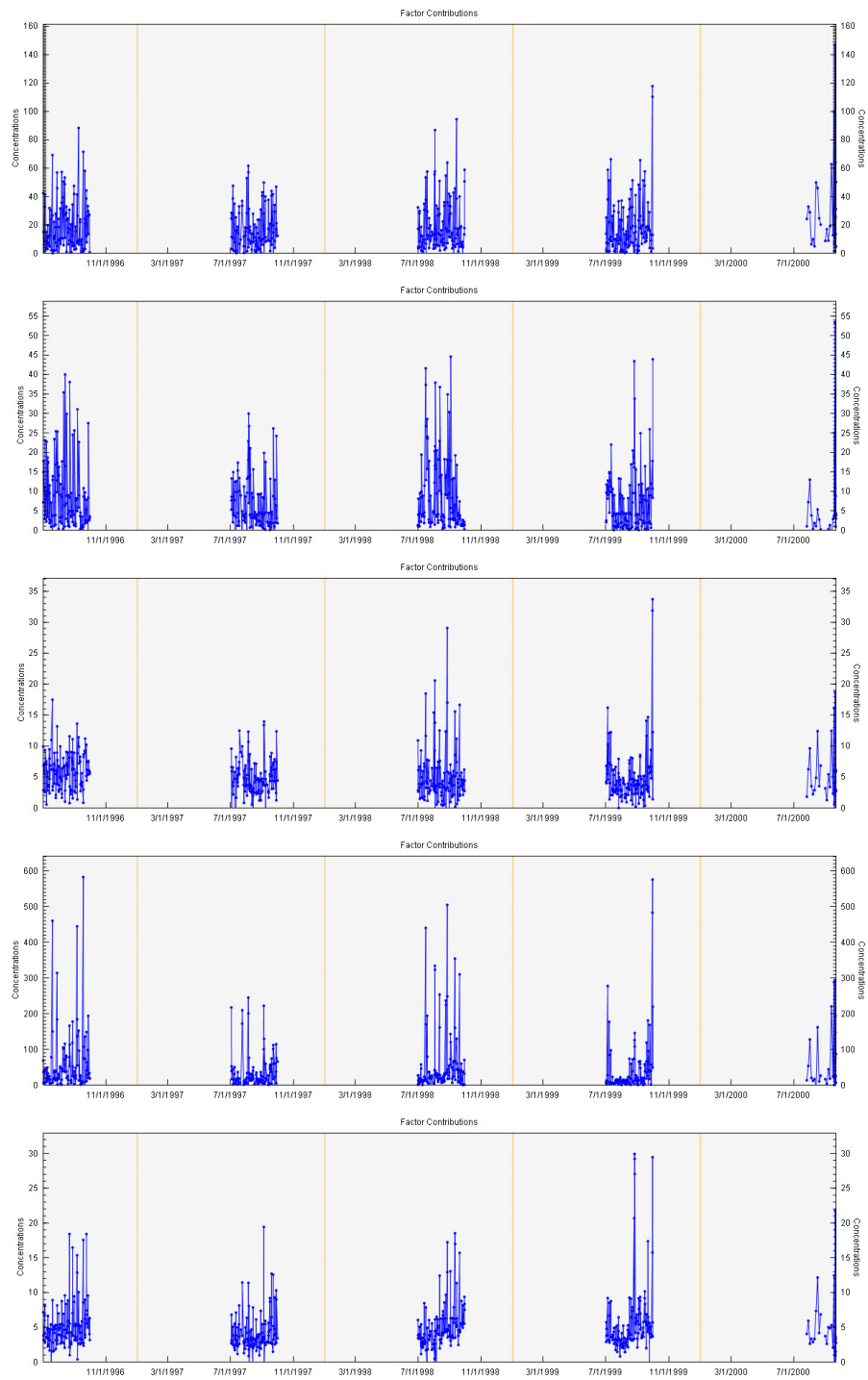


Figure A-6. Sacramento PMF factor contributions. From top to bottom: biogenic, coatings, mobile, mobile/aged, refinery/aged.